

## Experimental Error Estimates Associated with Pilot Activated-Carbon Investigations of Trace Organic Removals

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*The removal of trihalomethane precursor substances as estimated by total organic carbon using granular activated carbon was investigated in a pilot plant study. The study was designed with replicate GAC columns and replicate analytical procedures so that statistical statements could be made on postulated differences between column performances. After 55 days, the TOC removal mechanism appeared to be biological degradation, although the slow adsorption mechanism could not be ruled out. Grab and composite sampling should be evaluated for each granular activated-carbon study to avoid conclusions based on nonrepresentative data. Trihalomethane analytical variability dominated the variability of the overall experiment.*

THE METROPOLITAN WATER DISTRICT of Southern California (Metropolitan) is a public and municipal corporation of the State of California, which provides supplemental water as a wholesaler through 27 member agencies (cities and water districts) to nearly 12 million people in a 13,000-km<sup>2</sup> (4,900-sq. mi.) service area on the coastal plain of Southern California. Approximately one-half of this supplemental water— $860 \times 10^6$  m<sup>3</sup> (200,000 acre-ft)—is imported through 242 miles of aqueduct from the Colorado River. Initial deliveries of Colorado River water (CRW) began in 1941. In addition, Metropolitan has contracted to receive more than  $2,000 \times 10^6$  m<sup>3</sup> (2 million acre-ft) annually of Northern California water through the 444-mile-long State Water Project. First deliveries of State Project water (SPW) began in 1972.

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On November 29, 1979, the U.S. Environmental Protection Agency promulgated the trihalomethane (THM) regulation. The regulation established monitoring requirements and a maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes (total THM). Figure 1 shows a schematic of the feasibility analysis process that Metropolitan has been engaged in over the past few years in anticipation of the promulgation of the THM regulation. The schematic is very similar to a feasibility analysis schematic presented previously for control of synthetic organic chemicals (1). While the feasibility analysis process appears to be linear, several steps are being pursued in a parallel fashion.

Table I summarizes the extent of the trihalomethane problem in Metropolitan's system (2). Quarterly averages over the past 2.5 years have been very close to the MCL for total THM. What Table I does not show is that many member agencies take water from Metropolitan's system, hold it for several days, and possibly rechlorinate. Data from these systems are just now becoming available and, as expected, some member agency systems contain THM levels higher than the MCL. To meet its responsibility as a wholesale water purveyor, Metropolitan has embarked on a course of action to provide water to its member agencies that will allow them to comply with the MCL without additional treatment.

Changing the source of supply and using existing treatment processes to completely control the THM problem have been investigated and determined infeasible for Metropolitan. Other more exotic treatment techniques have been evaluated on a bench- and pilot-scale basis. In general, there are three ways to control trihalomethanes in drinking water: remove THM after formation, remove precursors before THM formation, and use a disinfectant other than chlorine to prevent THM formation.

This chapter focuses on research at Metropolitan dealing with the second option. The first option is not being seriously considered since the kinetics of THM formation in Metropolitan's case are relatively slow and removal of THM at the treatment plant is infeasible. Alternative disinfectants, particularly chloramines, are also being evaluated. The purpose of this chapter is to present the results of a study on the removal of THM precursor substances as estimated by total organic carbon using granular activated carbon (GAC). Data not included in this chapter have demonstrated a relationship between removal of THM precursors and removal of total organic carbon (TOC). Removals of individual THM components will also be discussed as examples of difficult to adsorb, low molecular weight halogenated methanes. The study was designed with replicate GAC columns and replicate analytical procedures so that statistical statements could be made on postulated differences between column performances.

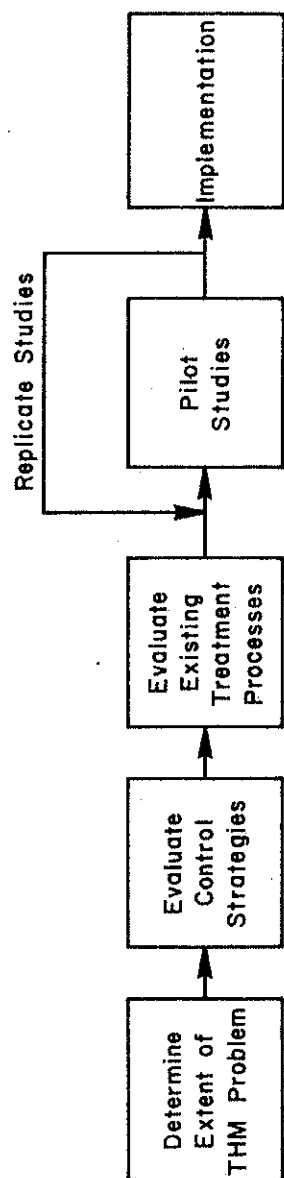


Figure 1. Feasibility analysis scheme for control of trihalomethanes.



Table I. Total Trihalomethane Data Summary

Quarter	Quarterly Average ( $\mu\text{g/L}$ )	Running Annual Average ( $\mu\text{g/L}$ )	Percent of Samples Over 100 $\mu\text{g/L}$
Jan. 1979	94	—	47
Apr. 1979	103	—	42
July 1979	114	—	64
Nov. 1979	97	102	47
Feb. 1980	79	98	8
May 1980	90	95	29
Aug. 1980	94	90	41
Nov. 1980	102	91	58
Feb. 1981	86	—	11
May 1981	80	—	18

### Experimental

TOC was analyzed in the water samples using a Dohrman DC-80 organic carbon analyzer. TOC removal was followed as a rough surrogate of the removal of THM precursors. In previous research at Metropolitan, a method had been developed to measure the THM formation potential by chlorinating a sample to a desired level, holding it over several weeks, and measuring the resulting THM compounds formed (3, 4). In an effort to improve pH control, a phosphate buffer was added to the samples in the GAC study prior to chlorination. Subsequently, it was discovered that the buffer was contaminated with a THM precursor, and all of the THM formation potential data had to be discarded.

Trihalomethane analyses were accomplished using a liquid-liquid extraction procedure followed by injection on a Varian 3700 gas chromatograph (2-4). Quality assurance procedures were rigorously employed in this work. Standards, spikes, replicates, and blanks accounted for 20-30% of the samples analyzed.

**Pilot Plant.** A 5-gallon/min all glass, stainless steel, and Teflon pilot plant was used to provide conventional treatment before GAC filtration. The pilot plant is located in a pipe gallery at the F. E. Weymouth Filtration Plant. Rapid mix, chemical addition, flocculation, sedimentation, and dual media filtration are the conventional unit processes.

Following a filtered water storage reservoir are six glass columns 15 cm (6 in) in diameter and 3 m (10 ft) high. Figure 2 illustrates how the columns were arranged during Phase I to test GAC in a parallel operations mode.

**Experimental Design and Sampling.** A number of pilot-scale GAC treatment studies have been completed (5). The studies are normally designed to investigate one or more of the following general parameters: comparison of adsorbents, effect of pretreatment, temporal variations of organics, hydraulic parameters, column operation modes, and removal of classes of organics.

Without exception, the studies have been conducted by comparing the results of one column versus another without any replication. There is no

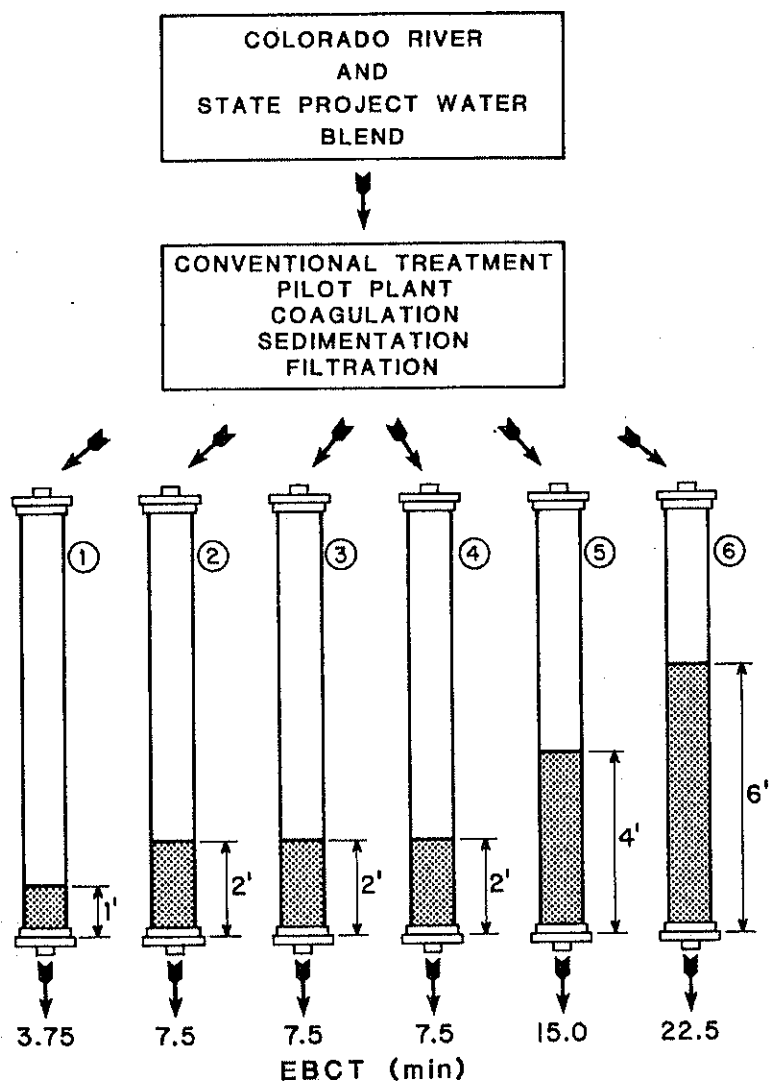


Figure 2. CAC pilot column arrangement in Phase I.

information available in the literature on estimates of the precision of these studies. It has been well established in the designs of most experiments that an estimate of the experimental error is essential to recognize significant differences between treatments (type of GAC, variation in hydraulic parameters, etc.). Until now, investigators relied on their "sense" of what a significant difference is. Of course, this "sense" varies among investigators and is a less than optimum method of decision making. There are a number of case histories in the literature that have produced conflicting conclusions on the effects of various parameters. While some of these conflicts are caused by real differences in the characteristics of the water being tested, it is suspected that some are the result of different "perceptions" of what a significant difference really is.

Another difficulty encountered in evaluating pilot plant data is the usual reliance on grab samples for characterizing the GAC column influent and effluent conditions (e.g., organic compound concentrations). Wide variability in influent/effluent conditions has made it difficult to interpret the actual mass loadings on the GAC columns. Diurnal, seasonal, and yearly variability of compound concentrations and water quality factors are rarely evaluated. Instead, one grab sample is assumed to be representative of an extended period of time (typically 1 week). One reason for the infrequent grab sampling scheme is the high cost and relatively involved analytical requirements for determining organic compounds in water. For the preceding reasons, it was decided to use composite samplers specially constructed for this project.

Figure 2 indicates that three replicate GAC columns with empty bed contact times (EBCTs) of 7.5 min were run in addition to three other columns with EBCTs ranging from 3.75 to 22.5 min. Influent and effluent composite samples were collected using the sampler designed by Westrick and Cummins (6). Grab samples were also collected and compared to the respective composite sample results. The composite samplers were designed to ensure a headspace free sample with no significant losses of volatile trace organic compounds (e.g., trihalomethanes) over the 3.5-day compositing period. The samplers were kept in refrigerators to preserve the sample.

It was anticipated that, over the course of the project period, the quality of the pilot plant influent water would vary considerably. The pilot plant receives the same blend of State Project and Colorado River water that the F. E. Weymouth Filtration Plant receives. Figure 3 shows how the percentage of SPW changed over the project period. The dramatic fluctuations were caused by requirements to shut down either the SPW or CRW system for scheduled preventative maintenance. The purpose of using the composite samplers was to obtain representative samples during the fluctuation periods. While it is true that composite sampling masks the peaks and valleys, it does give an accurate average representation of what a population might be exposed to over a period of time. This is the type of information that toxicologists and epidemiologists require to evaluate a population's exposure to potentially harmful compounds.

**Statistics.** A variety of statistical techniques were used to evaluate significant differences between the GAC column performances (7, 8). Analysis of variance, unpaired *t* test, *F* test, and confidence limits were calculated on influent and GAC column effluent data. In addition, the variance associated with the total experiment was partitioned into the analytical and column variances. From statistical theory we can write:

$$\sigma_{\text{total}}^2 = \sigma_{\text{analytical}}^2 + \sigma_{\text{column}}^2 \quad (1)$$

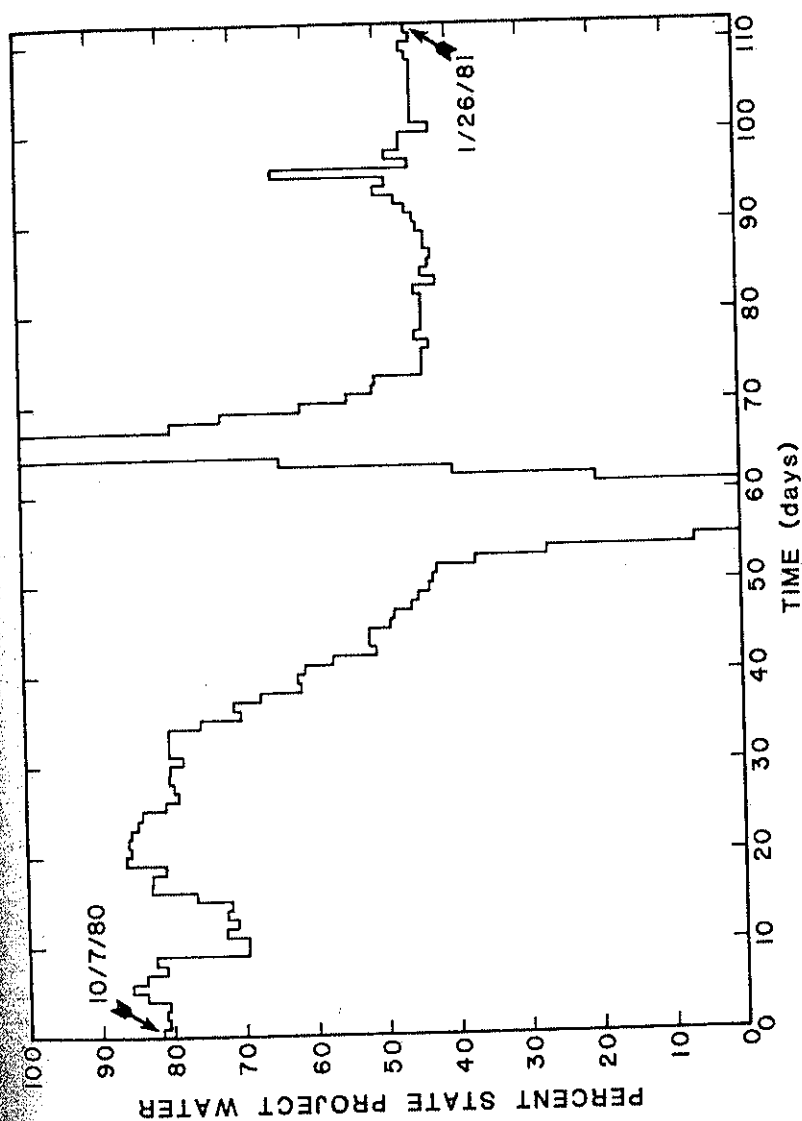


Figure 3. Percent State Project water in pilot plant influent.



This equation is only valid if  $\sigma_{\text{analytical}}^2$  and  $\sigma_{\text{column}}^2$  are statistically independent.

Equation 1 was applied to the breakthrough data from the three 7.5-min EBCT columns to obtain the total variance,  $\sigma_{\text{total}}^2$ , and to the analytical precision data to obtain the analytical variance,  $\sigma_{\text{analytical}}^2$ . The variance associated with running the columns,  $\sigma_{\text{column}}^2$ , was calculated by subtraction. The purpose of this exercise was to determine which part of the experiment contributed to the majority of the experimental variance.

### Results and Discussion

**TOC Removals.** Variability in the influent TOC data was tested over a 24-h period on December 11 and 12, 1980. Figure 4 shows little variability in the hourly grab samples of the column influent. These data are confirmed in Figure 5 which shows the influent and GAC column effluent TOC data. These data and all subsequent data, unless noted, are derived from composite samples. The influent TOC data are remarkably consistent despite the wide variations in percent blend shown in Figure 3. The TOC content of the two sources of supply was very similar during the Phase I testing period.

The GAC column effluent data in Figure 5 show the classic breakthrough pattern for TOC: (1) immediate low level leakage through the columns, (2) regular, orderly breakthrough during the first phase, followed by (3) a pseudo steady-state.

Figure 6 illustrates the pseudo-steady-state more clearly by the parallel cumulative removal curves. Previous discussions regarding pseudo-steady-state removal have relied on a discussion of biological activity to explain the phenomenon. Recently, an alternate explanation involving the slow adsorption mechanism has been proposed (9). There is direct evidence to support a biological activity mechanism including elevated standard plate counts in GAC column effluents, high bacterial densities measured by standard plate counts on the exhausted carbon surface, and direct observation of bacterial species on the carbon surface.

Figure 7 is a scanning electron photomicrograph of the surface of one granule of activated carbon from Phase I. Visible are cocci, spirillum, and filamentous bacteria.

After the completion of the pilot study, bacteria were washed from the carbon surface, isolated on plate count media, and identified to the genus level using the three-tube technique of Lassen (10). The dominant genera recovered from the carbon surface included *Pseudomonas* and *Moraxella* with some *Micrococcus* and other unidentified bacteria.

The alternate explanation for at least part of the pseudo-steady-state removal of TOC has been described as "slow adsorption" (9). The phenomenon is said to be caused by the large size of the humic acid molecules that are difficult to fit into the much smaller pore system of



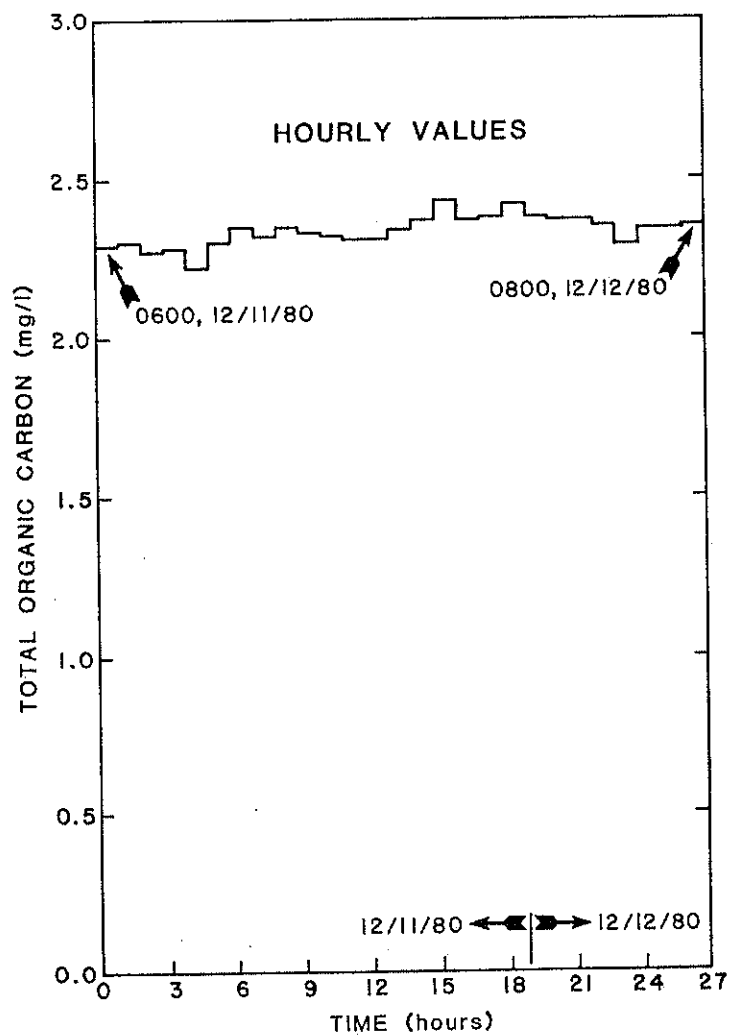


Figure 4. Total organic carbon at GAC/carbon influent; pilot I.

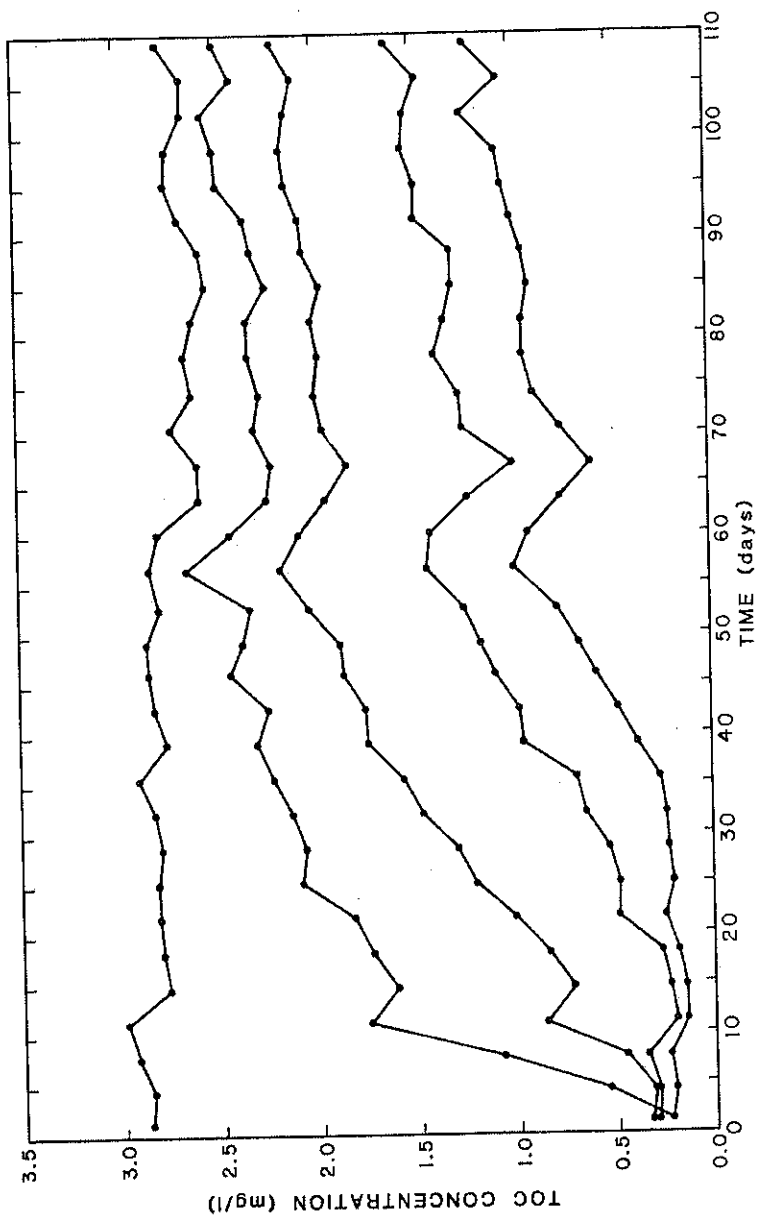


Figure 5. Breakthrough curves for total organic carbon; pilot 1 composite samples. Key reading from top to bottom: influent, EBCT = 3.75 min, EBCT = 7.5 min (mean of 3 replicates), EBCT = 15 min, and EBCT = 22.5 min.

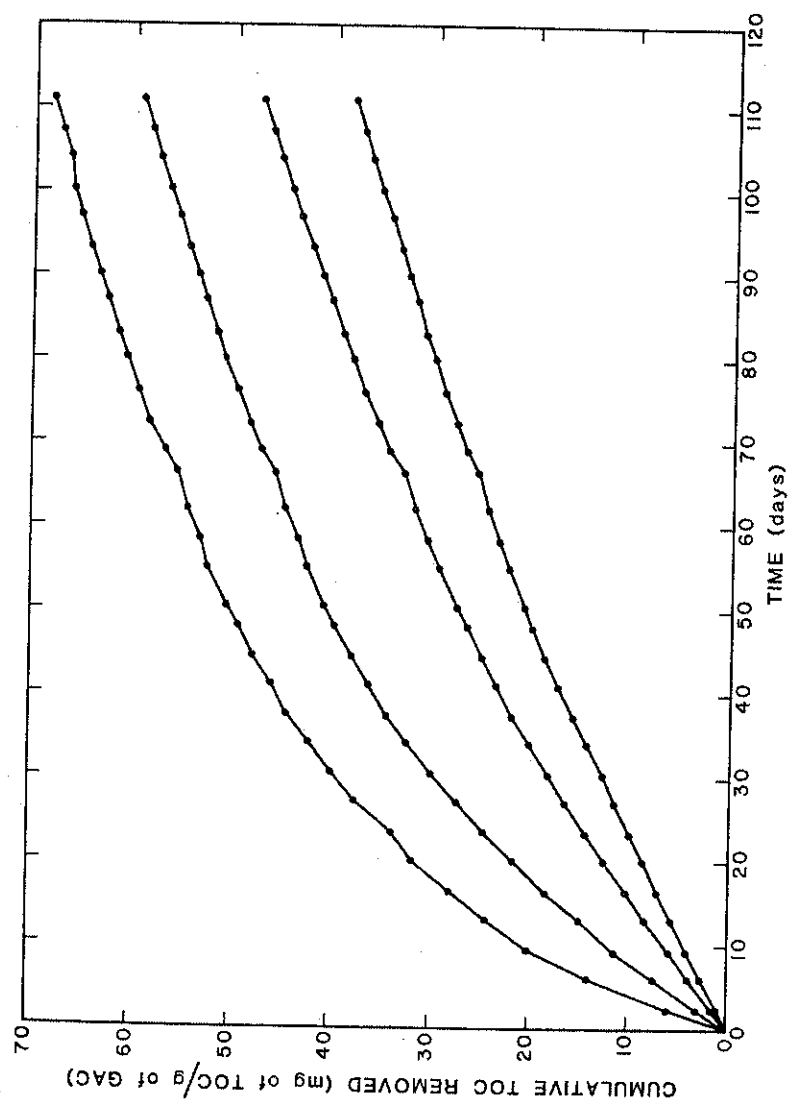
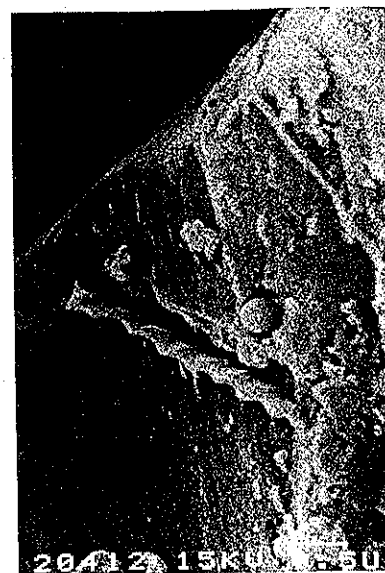


Figure 6. Cumulative removal of total organic carbon; pilot 1. Key reading from top to bottom: EBCT = 3.75 min, EBCT = 7.5 min (mean of 3 replicates), EBCT = 15 min, and EBCT = 22.5 min.



*Figure 7. Scanning electron photomicrograph of bacteria on surface of activated-carbon granule (28,00)XL).*



activated carbon. Thus, the long-term kinetics of humic acid-like molecules are slow and account for at least part of the plateau regions of the breakthrough curves.

Table II presents a summary of the TOC removal data for the pseudo-steady-state period (Days 55–110). The amount of TOC removed per gram of carbon appears to be consistent in the GAC columns except for the 15-min EBCT. The surface applied rate for all six of the GAC columns was 2 gallons/min/ft<sup>2</sup> at the beginning of the test. However, the column with an EBCT of 15 min lost 25 cm (10 in.) of activated carbon during one backwash cycle. To keep the EBCT the same, it was necessary to reduce the surface applied rate to 1.5 gallons/min/ft<sup>2</sup>. This lower surface applied rate appeared to increase TOC removal on a per gram of carbon basis. Whether this is due to bacterial activity or “slow adsorption” is not clear. Other work has shown that compounds removed by a strictly adsorption mechanism are not affected by variations in linear velocity (11).

Figure 8 illustrates the excellent replication of the TOC breakthrough data for the three 7.5-min EBCT results. Based on a two-way ANOVA test, the TOC breakthrough curves for EBCT values of 3.75, 7.5, 15.0, and 22.5 min were judged to be significantly different.

**Trihalomethane Removals.** Figure 9 illustrates the total THM results of hourly grab samples of GAC column influent compared to a 24-h composite sample collected during the same time period. The significant diurnal variation in total THM values illustrated the need for composite

Table II. TOC Removal Summary

EBCT (min)	Carbon Depth (ft)	Amount TOC Removed Days 55-110 (mg/g)
3.75	1	15.8
7.5	2	16.9
15.0	4	18.1
22.5	6	15.9

sampling. There is no significant difference (based on 95% confidence intervals) between the composite value of 46  $\mu\text{g/L}$  and the mean of the hourly values of 42.6  $\mu\text{g/L}$ .

The more highly variable nature of THM is clearly demonstrated in Figure 10 which shows the influent values and breakthrough curves for chloroform. On a percentage basis, the influent variability of chloroform is significantly greater than that of TOC shown on Figure 5. The chloroform breakthrough curves are also not as "smooth" as the TOC breakthrough curves. The influence of EBCT is demonstrated by the progressively longer time for chloroform breakthrough and exhaustion for each breakthrough curve.

Breakthrough curves for the three other trihalomethanes are shown in Figures 11-13. As bromine substitution increases on the methane molecule, the adsorption of the compound progressively improves. Breakthrough times for the four trihalomethanes for the 3.75-min EBCT were 11, 18, 32, and 49 days, respectively. Traces of bromoform did appear prior to breakthrough; however, this is the usual pattern for trace and highly variable influent organic compound concentrations.

Figure 14 illustrates the increased variability in the 7.5-min EBCT replicate breakthrough curves for chloroform as compared to those for TOC (see Figure 8). Also, Figure 14 demonstrates that the effluent chloroform concentrations from all three replicate columns appear to be in excess of the influent concentration on a consistent basis after exhaustion at 39 days. A statistical examination ( $t$  test) of the mean breakthrough data for the 7.5-min EBCT column and the influent chloroform concentration established that there was a significant difference at 0.05  $\alpha$  level. This observation is one more illustration of the chromatographic effect discussed elsewhere (12, 13). Poorly adsorbed compounds like chloroform are desorbed from the carbon surface by other more strongly adsorbed trihalomethanes or strongly adsorbed fractions of the TOC.

While there was significant variability in the influent chloroform data, a comparison of grab versus composite sample results shown in Figure 15 suggests no significant difference between the two data sets. A  $t$  test at the 0.05  $\alpha$  level confirmed the graphical observation. Justifying these results

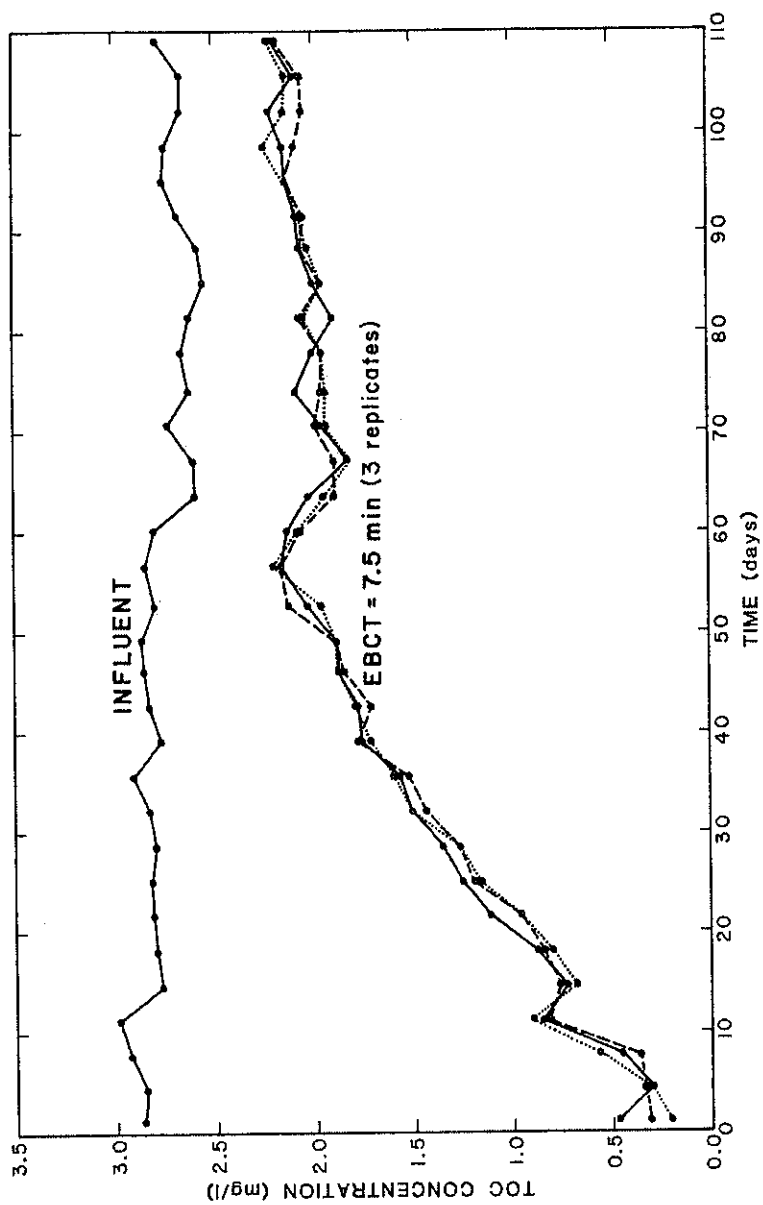


Figure 8. Breakthrough curves for total organic carbon; pilot 1 composite carbon; pilot 1 composite carbon; pilot 1 composite carbon. Comparison of three replicates. Key reading from top to bottom: influent, and EBCT = 7.5 min (3 replicates).



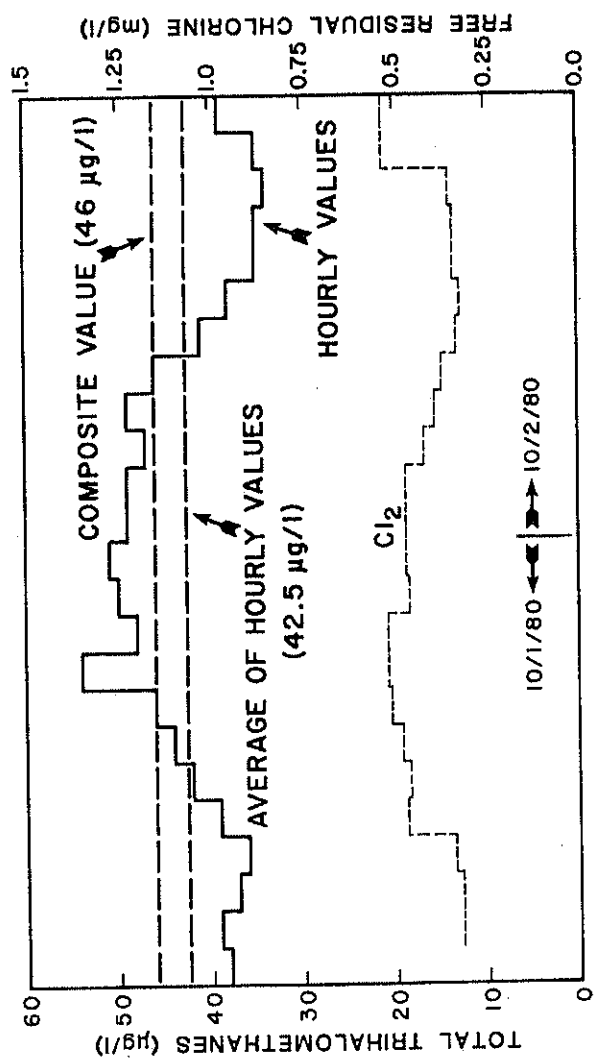


Figure 9. Hourly grab samples versus 24-h composite sample; pilot 1. Total trihalomethanes in CAC column influent.

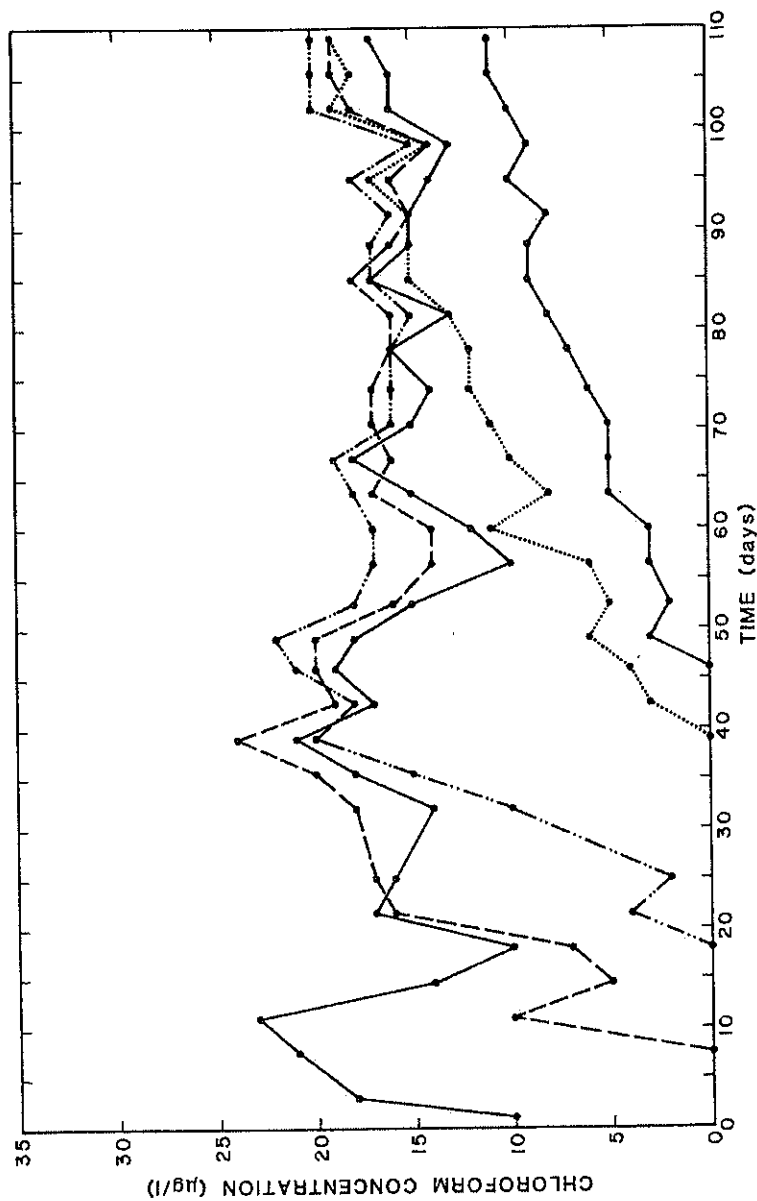


Figure 10. Breakthrough curves for chloroform; pilot 1 composite samples. Key reading from left to right: influent, EBCT = 3.75 min, EBCT = 7.5 min (mean of 3 replicates), EBCT = 15 min, and EBCT = 22.5 min.

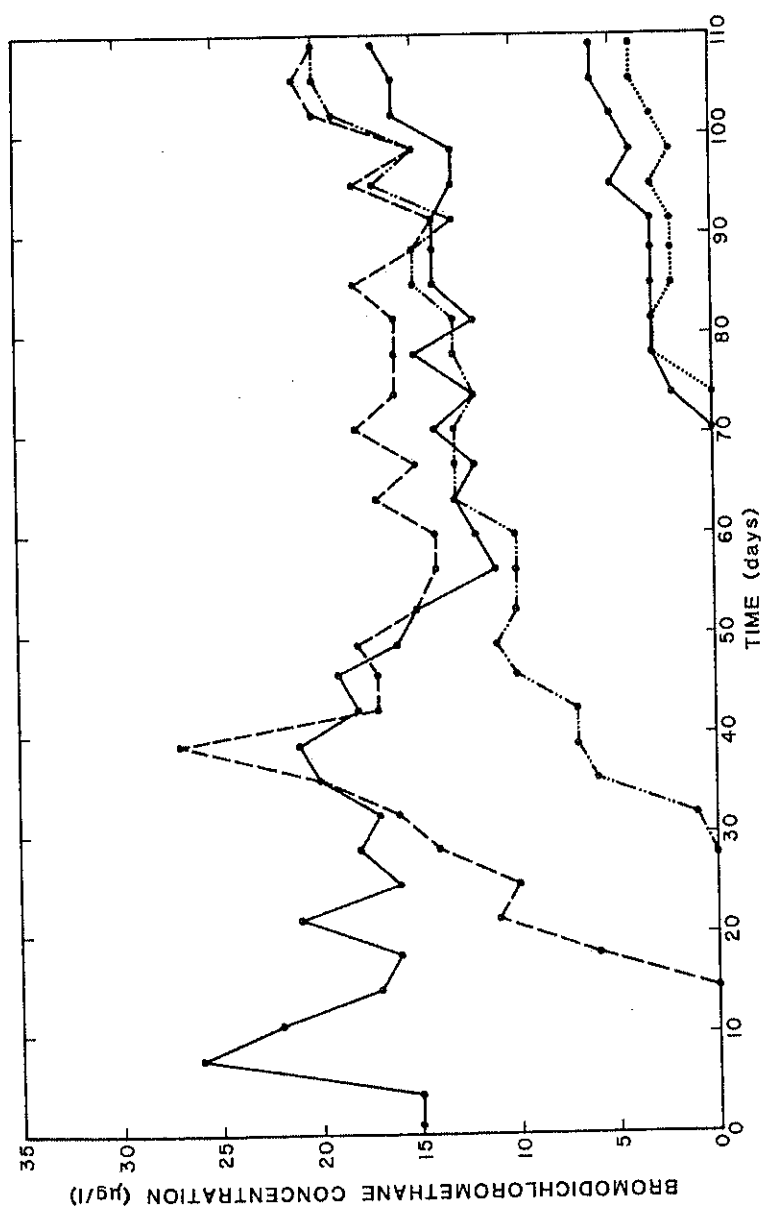


Figure 11. Breakthrough curves for bromodichloromethane; pilot 1 composite samples. Key reading from left to right: influent, EBCT = 3.75 min, EBCT = 7.5 min (mean of 3 replicates), EBCT = 15 min, and EBCT = 22.5 min.



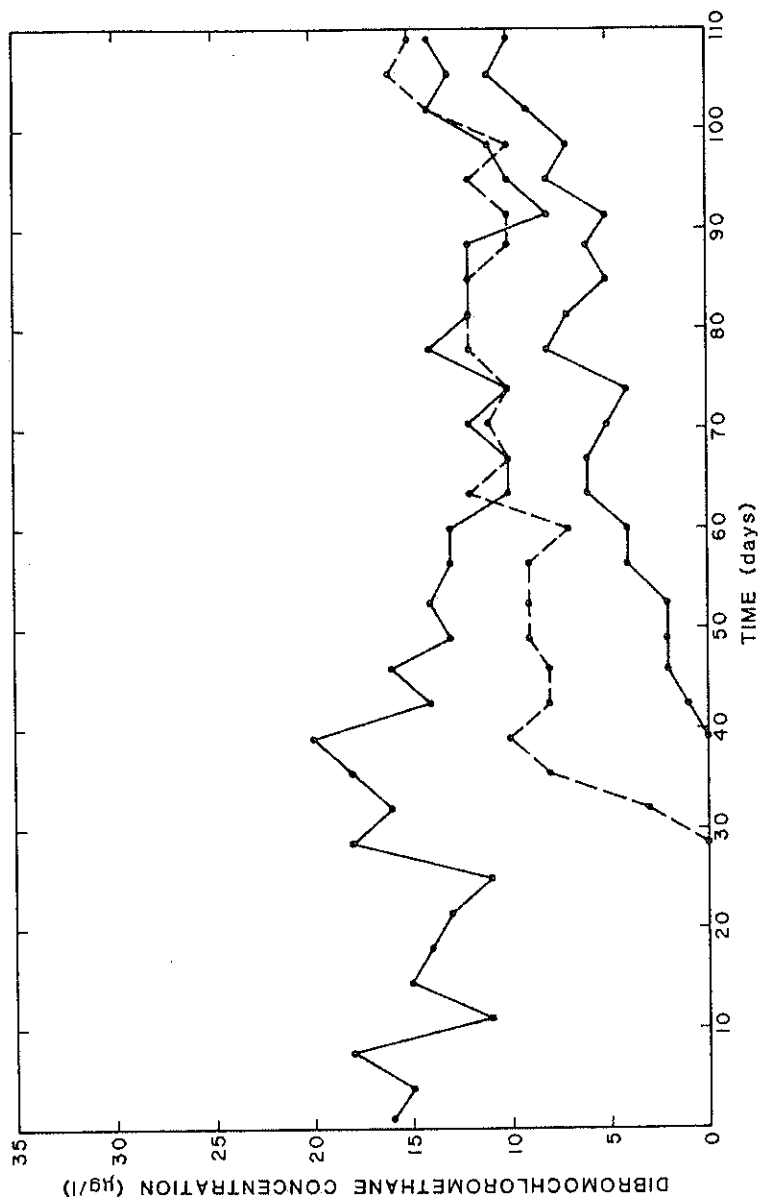


Figure 12. Breakthrough curves for dibromochloromethane; pilot 1 composite samples. Key reading from top to bottom: influent, EBCI = 3.75 min, and EBCI = 7.5 min (mean of 3 replicates).

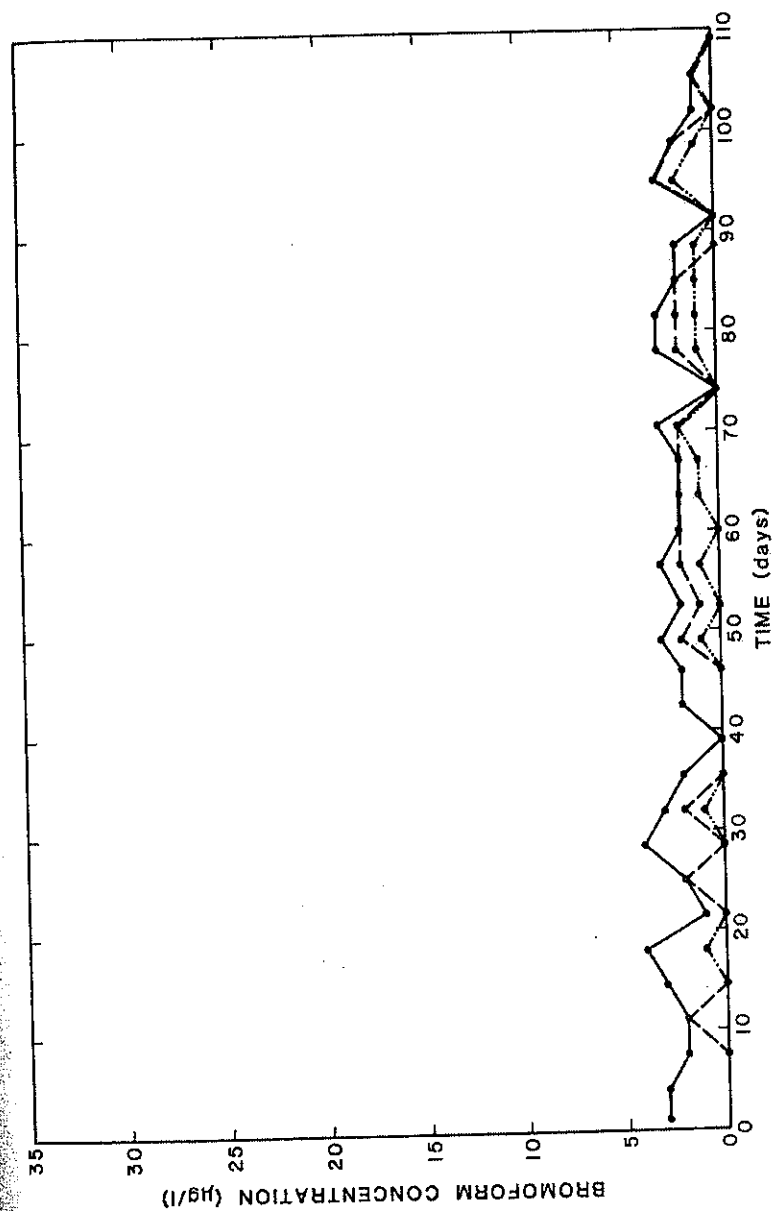


Figure 13. Breakthrough curves for bromoform; pilot 1 composite samples. Key: ●—● influent; —●—●, EBCT = 3.75 min; and —●—●, EBCT = 7.5 min (mean of 3 replicates).

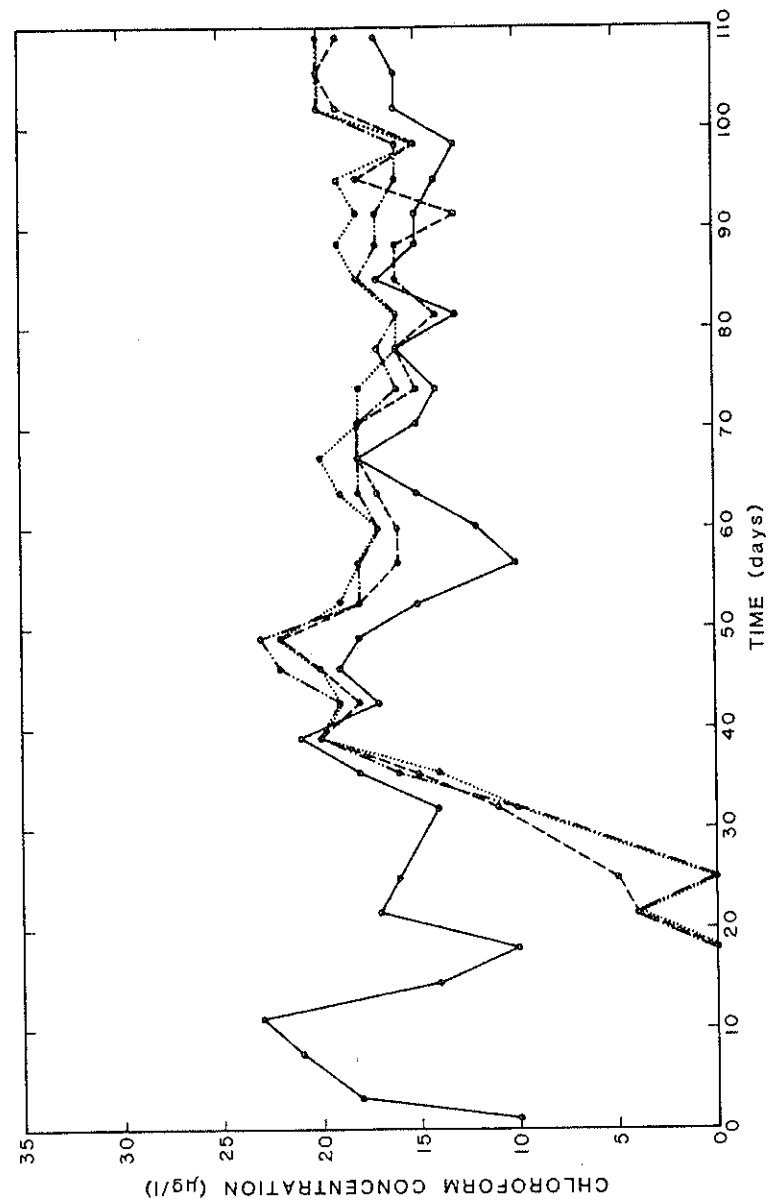


Figure 14. Breakthrough curves for chloroform; pilot 1 composite samples. Comparison of three replicates. Key: upper curve, influent, and lower curves, EBCT = 7.5 min (3 replicates).



with the significant diurnal variation shown in Figure 9 is not straightforward. It appears that the grab samples were taken at a time during the day that was more or less representative of the 3.5-day composite value. It must be assumed that this is particular to Metropolitan's system and should not be extrapolated to other systems. Every GAC column study should evaluate the need for composite sampling particularly if the removal of highly variable synthetic organic chemicals is a major objective of the project.

**Variance Estimates.** Table III lists the variance distribution and coefficients of variation for the five parameters studied in this project. The total variance for the THM compounds appears to be almost exclusively composed of the analytical variance. The anomalous results for  $\text{CHClBr}_2$  indicate that, for this compound, the analytical variance estimated from the replicate determinations was not a good estimate.

The TOC variance data show that the total variance is composed primarily of the variance associated with running the parallel columns. However, as Figure 8 illustrated, the overall variance is extremely low from a practical point of view. The TOC analytical method is much more precise than the individual THM analyses.

To make comparisons between the total variances for the five parameters, the coefficients of variation were calculated. This statistic was calculated by dividing the square root of the total variance by the overall mean of the breakthrough curve data for the 7.5-min EBCT curves. Table III indicates that the coefficient of variation for the TOC data was at least half of the variation of the THM data. The high bromoform value is the result of dividing by a small overall mean. Figure 13 showed that the bromoform results were generally much lower than the other three THM compounds.

For analyses that are inherently imprecise, such as THM compounds, the total variance was almost exclusively associated with the analysis. Results shown on Table III indicated low relative values for  $\sigma_{\text{column}}^2$  which suggests that excellent hydraulic control was maintained throughout the pilot plant. In the design of the pilot plant, a reliable hydraulic design was

Table III. Variance Distribution Summary

Compound	$\sigma_{\text{total}}^2$	=	$\sigma_{\text{analytical}}^2$	+	$\sigma_{\text{column}}^2$	Coefficient of Variation (%)
$\text{CHCl}_3$	1.17	=	1.15	+	0.02	6.6
$\text{CHCl}_2\text{Br}$	1.00	=	0.91	+	0.09	7.8
$\text{CHClBr}_2$	0.31	≠	0.79	+	—	8.7
$\text{CHBr}_3$	0.48	=	0.46	+	0.02	80.6
TOC	0.003	=	0.00084	+	0.00216	3.3

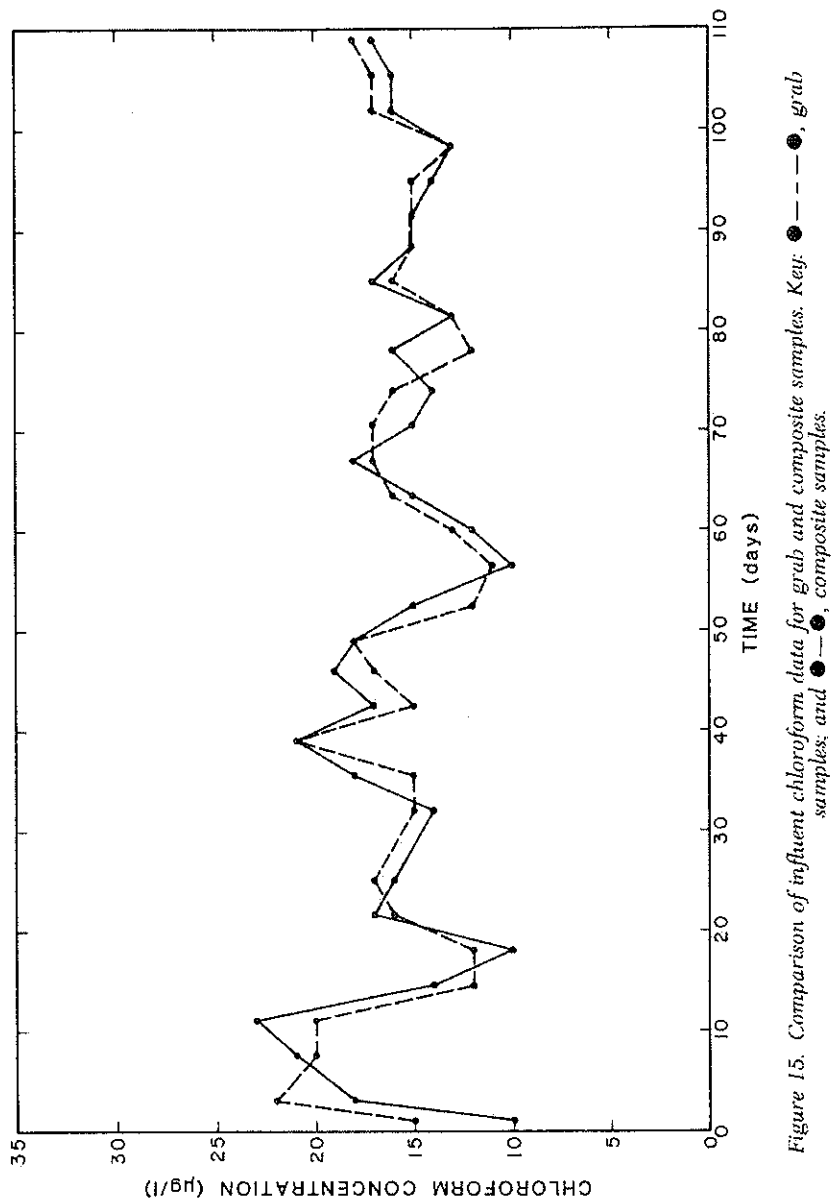


Figure 15. Comparison of influent chloroform data for grab and composite samples. Key: ●—, grab samples; and ●—, composite samples.

recognized as critical to the overall performance of the research studies. It appears that care in hydraulic design has paid off in stable, reproducible results.

### *Summary and Conclusions*

Replication of GAC columns and analytical results is critical if statistically significant results are to be determined.

TOC removal appears to be affected by linear velocity. It is expected from other work that removal of compounds affected primarily by adsorption is not affected by linear velocity. The linear velocity effect will be tested in upcoming experiments.

After 55 days, the TOC removal mechanism appears to be biological degradation, although the "slow" adsorption mechanism cannot be ruled out. More site-specific and mechanistic investigations are needed of the "slow" adsorption phenomenon and its contribution to pseudo steady-state removal of TOC.

The chromatographic effect for chloroform was demonstrated to be statistically significant. The more poorly adsorbed compound is preferentially desorbed by the other more highly adsorbed compounds.

Grab and composite sampling should be evaluated for each GAC treatment study to avoid conclusions based on nonrepresentative data.

The results of the Phase I study showed that the predominant variability of the replicate columns was caused by analytical variability for THM compounds. TOC results were demonstrated to be much more precise than the THM results.

### *Acknowledgments*

The work of Edward G. Means in identifying bacterial genera on the carbon surface and in producing the electron photomicrograph is gratefully appreciated.

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## RESEARCH &amp; TECHNOLOGY

# AWWARF Trihalomethane Survey

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This survey was conducted to determine the extent and costs of compliance with the existing maximum contaminant level (MCL) for trihalomethanes (THMs). It was found, on average, that the MCL of 0.10 mg/L had reduced the concentrations of THMs in larger utility systems by 40-50 percent. About 4.6 percent of the responding utilities had exceeded the MCL at least once during the period 1984-86. Compliance with the THM regulation involved estimated capital expenditures of \$31-102 million and yearly operating and maintenance costs of \$8-29 million for utilities serving more than 10,000 people. Approximately 75 percent of the water quality managers responding believed that the MCL should not be reduced below 0.10 mg/L. Only four states require that smaller utilities (those serving fewer than 10,000 people) monitor for THMs.

On Nov. 29, 1979, the trihalomethane (THM) maximum contaminant level (MCL) of 0.10 mg/L was promulgated by the US Environmental Protection Agency (USEPA).<sup>1</sup> This MCL was based primarily on technical feasibility, and the

USEPA has clearly indicated that it intends to lower the MCL significantly.

On June 19, 1986, amendments to the Safe Drinking Water Act were signed into law. In accordance with the timetable set by Congress, the USEPA an-

nounced that it intends to set new MCLs for disinfection by-products, including THMs, as part of the first group of 25 regulations due to be finalized by 1991.

This article presents the results of a national survey of THMs in drinking water and determines the extent and costs of compliance with the existing THM regulation. This survey is expected to form the basis for determining the costs and feasibility of compliance by the industry with a new regulation.

The idea for the THM survey was developed by a committee of the Association of Metropolitan Water Agencies. The survey was carried out by the Metropolitan Water District of Southern California (Metropolitan) and Decision Research, under partial funding by a contract with the AWWA Research Foundation (AWWARF).

## Utility questionnaire

This study determined that no comprehensive national THM data base was in existence at the USEPA, AWWA, or any other national organization. All primary agencies (states and the USEPA) have THM records for the water utilities whose compliance they supervise, but obtaining the data from files or from noncompatible data bases was deemed an inefficient survey method. Moreover, data available through such an approach would not include the costs of reaching the recorded THM concentrations.

Because every water utility serving a population of more than 10,000 people is required to monitor for THMs, a questionnaire was designed and sent directly to selected utilities, requesting information on THMs and on meeting the THM

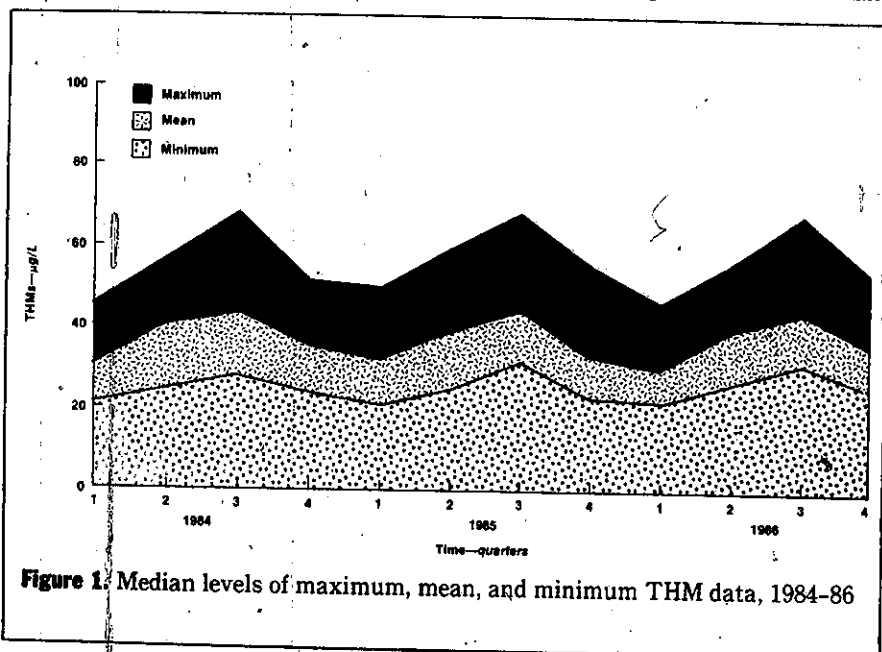


Figure 1. Median levels of maximum, mean, and minimum THM data, 1984-86

regulation. The questionnaire was prepared by Decision Research in consultation with water utility experts as well as USEPA representatives. In the final version of the questionnaire, each respondent was asked:

(1) to provide water supply and treatment information, including the utility's source of water, number of treatment plants, treatment capacity, types and dosages of chemicals used, type of ownership, wholesale and retail populations served, amount of treated water sold, and cost of water;

(2) to complete a log of quarterly total THM concentrations (mean, maximum, and minimum) from 1984 through 1986 and to indicate whether or not a public notification of violation of the THM regulation was ever required;

(3) to state (a) whether treatment was modified or supplies were changed to meet the 0.10-mg/L MCL and (b) the cost of meeting that regulation;

(4) to indicate whether the utility had problems with taste and odor, corrosion, color, microbiological quality, or biofilm growth as a result of modifying treatment to meet the 0.10-mg/L MCL;

(5) to estimate both the capital and the operating and maintenance costs of meeting 50-, 25-, and 5- $\mu$ g/L MCLs for THMs, the method likely to be used to meet these lower MCLs, and the basis for the estimate;

(6) to state an opinion as to whether the MCL should be lowered to less than 0.10 mg/L;

(7) to answer a series of questions on water system concentrations of trihalomethane formation potential (THMFP), bromide, total organic carbon (TOC), color, total organic halogen (TOX), dihaloacetonitrile (DHAN), and other disinfection by-products;

(8) to answer a series of questions on monthly turbidity averages for measurement of filtration plant performance (not reported in this article); and

(9) to respond to questions on whether additional research was required on treatment for THMs, analytical methods, filtration research, or other topics.

**Sampling procedures.** The group surveyed consisted of three samples selected from water utilities serving more than 10,000 customers. (These utilities are the only ones required to report THM data.) According to the USEPA, there are 3,081 utilities that serve more than 10,000 customers, with a total of 171 million people being served by these systems.

First, all utilities serving more than 50,000 customers were included in the survey. Previously collected data showed that there were 600 such utilities in the United States, serving approximately 57 percent of the population. Second, approximately half of the utilities serving

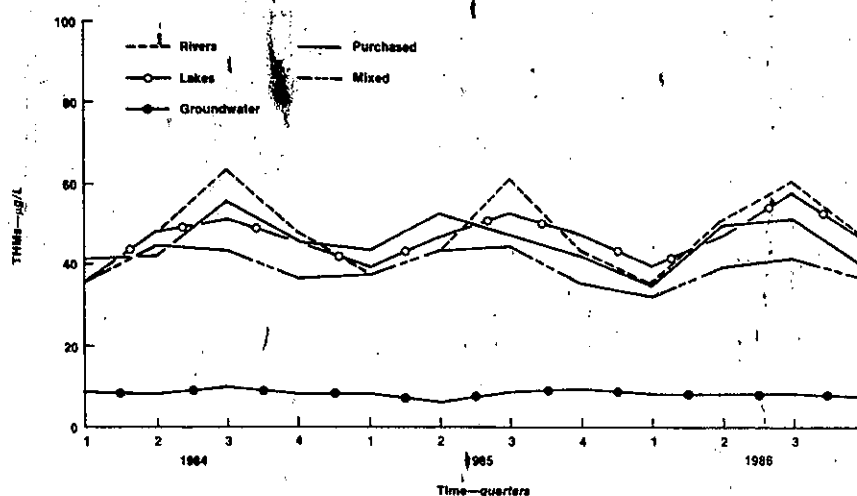


Figure 2. Median THM levels by source of supply

TABLE 1  
Quarterly mean THM data for three utility size categories by source of supply

Source of Supply	Overall THM Mean— $\mu$ g/L		
	10,000-25,000	25,000-50,000	>50,000
Rivers	60	56	49
Lakes	64	59	44
Ground	21	20	22
Purchased	61	44	49
Mixed	37	42	47

between 25,000 and 50,000 customers were surveyed. Of an estimated total of 700 such utilities, representing 5.3 percent of the population served, 318 were sent surveys. These 318 utilities were chosen from the Federal Reporting Data System (FRDS) through a computerized random-selection process. Finally, about 20 percent, or 387, of the 1,750 systems serving between 10,000 and 25,000 customers (2.4 percent of the population) were chosen from the FRDS, again by random selection. Overall, 1,255 eligible utilities were sent questionnaires.

The questionnaires were addressed to the water quality manager at each utility. Analysis of the returns, however, showed that many different officials, ranging from the general manager to the water quality laboratory supervisor to the treatment plant operator, actually completed the questionnaires.

**Mailing procedures.** Although the FRDS data base contained the data classifications of the three system sizes, the

mailing addresses given were not as current as those on the AWWARF mailing lists. The AWWARF generated mailing labels for all utilities in the three size categories, which were then hand-matched to the sample selected from the FRDS list. For cases in which utilities' names appeared on the FRDS list but not on the AWWARF lists, new mailing labels were prepared.

The utilities were sent either two or three mailings. One week before the questionnaires were mailed, an oversized postcard was sent via first-class mail to the water quality manager at each selected utility. The postcards were mailed on Jan. 6, 1987, and indicated that a certified letter and questionnaire would soon follow.

The questionnaires were mailed via certified mail on Jan. 14, 1987. Each questionnaire and return envelope was stamped with a number code matched to the master list. The packet included a cover letter, the questionnaire, and the

**TABLE 2**  
*Treatment changes made by utilities to comply with 0.10-mg/L MCL*

Treatment Change	Number of Treatment Changes	
	AAWARP Study	TBS-MP* Estimate
Procedure modification		104
Improve clarification	41	
Change chlorine dosage	122	
Change point of disinfection	150	
Chloramines	100	91
Chlorine dioxide	26	18
Powdered activated carbon	25	9
Off-line storage	4	1
Alternate source	2	1
Aeration	9	4
Install clarification	4	1
Ozone	3	1
Granular activated carbon	10	
Other	47	
Total	543	242

\*Temple, Barker & Sloane Inc. and Malcom Pirnie Inc.\*

**TABLE 3**  
*Capital costs of complying with the 0.10-mg/L MCL*

Treatment Change	Capital Cost—\$ million	
	AAWARP Study	TBS-MP Estimate*
Procedure modification		6.921
Improve clarification	1.7 (15)*	
Change chlorine dosage	0.05 (42)	
Change point of disinfection	0.7 (67)	
Chloramines	8.8 (64)	8.781
Chlorine dioxide	0.4 (19)	2.069
Powdered activated carbon	0.1 (11)	0.814
Off-line storage	0 (1)	4.154
Alternate source	0 (0)	7.909
Aeration	1.7 (5)	9.717
Install clarification	8.0 (2)	5.419
Ozone	1.7 (3)	2.294
Granular activated carbon	0.3 (5)	
Other	7.6 (34)	
Total	31 (268)	47.448

\*The number in parentheses is the number of utilities that provided cost data in this category of treatment change.

percent, meaning that in 95 percent of all samples drawn from the same population, the findings would not differ from the reported findings by more than 6 percent. The subsamples, however, were much smaller, and a greater error range occurred when the questions were broken down by utility size for more detailed analysis.

Although the authors are confident that Metropolitan's questionnaire review resulted in higher quality data, the data must still be viewed cautiously. "Impossible" values outside the normal range may have escaped detection if the questionnaire was otherwise fully completed. A very common error was the respondent's failure to specify whether treatment procedures had been changed to meet the 0.10-mg/L THM regulation. Many respondents (despite the instructions) left blanks instead of circling the "no" response. Thus, for analysis of the question on treatment changes, the absence of any indication of change has been defined as a "no" answer rather than as missing data.

The survey results were also limited by the large number of missing data entries, particularly for cost estimates. In general, the larger utilities provided more comprehensive answers. The results for many of the cost and expenditure questions, therefore, were potentially skewed toward the results provided by the larger utilities.

Errors resulting from missing data were more problematic than sampling errors. For each group of different-sized utilities, the response rate and large sample size assured generalizability. Therefore, the authors are confident that the data present a true picture of the state of the water industry. The data must be interpreted cautiously, however, because a lack of uniform standards of reporting, recordkeeping, and technical sophistication has raised concerns about the overall data quality.

#### State questionnaire

Because a new THM regulation could possibly be applied to utilities serving fewer than 10,000 customers, an attempt was made to gather representative data from the more than 55,000 water utilities in this size category. A simple questionnaire was sent to all states and territories to determine whether THM monitoring and MCL compliance are required for smaller utilities. The states were asked to send summarized THM data, if available, on their smaller utilities.

Mail responses were received from a majority of the states and territories. Followup telephone calls resulted in an eventual 100-percent response from regulatory agencies in the states and territories. The THM data received from the states were reviewed for consistency

numbered, postpaid business reply envelope. The questionnaires were clearly marked with a January 27 return date.

**Questionnaire handling.** Returned questionnaires were logged by number code to ensure anonymity and were then reviewed for completion. Open-ended questions were coded for computer entry, and a list of wholesale suppliers was developed. Most questionnaire results can be directly keypunched, but in the case of the THM questionnaires this was not possible. The questionnaire instructions were not carefully followed, and many of the returned questionnaires included only partial data—or no data at all—for even the most basic questions (population served, total water sold, names of wholesale water suppliers, and so forth). Because many utilities failed to provide the data on population served, their sizes were determined from the AWWARF and FRDS lists.

All questionnaires containing unusual data or missing important data were

turned over to Metropolitan's Water Quality Laboratory for review. Laboratory personnel either converted the non-standard results to uniform scales or called the respondent for further information. Overall, only 29 percent of the questionnaires could be entered into the computer system without further review, whereas 71 percent required some intervention.

**Limitations of the survey.** The sampling and research procedures employed in the survey were subject to the normal statistical and nonstatistical errors of survey research. Nonstatistical errors result from dishonest responses, transcription errors, inconsistency between expressed attitudes and actual behaviors on opinion questions, and misunderstood questions.

Normally, the sizes of the two samples—10,000–25,000 and 25,000–50,000 customers (the more-than-50,000 category is the population, not a sample)—would provide an error range of  $\pm 6$



**TABLE 4**  
*Operating and maintenance costs of complying with 0.10-mg/L MCL*

Treatment Change	Operating and Maintenance Cost—\$1,000	
	AWWARF Study	TBS-MP Estimate*
Procedure modification		6,033
Improve clarification	2,600 (21)*	
Change chlorine dosage	80 (42)	
Change point of disinfection	130† (49)	
Chloramines	1,300 (57)	5,018
Chlorine dioxide	1,200 (15)	1,694
Powdered activated carbon	85 (14)	1,934
Off-line storage	0 (0)	132
Alternate source	6 (1)	563
Aeration	110 (4)	1,496
Install clarification	58 (1)	91
Ozone	27 (1)	197
Granular activated carbon	270 (6)	
Other	2,500 (30)	
Total	8,106 (241)	17,158

\*The number in parentheses is the number of utilities that provided cost data in this category of treatment change.

†Cost savings of \$130,000

**TABLE 5**  
*Cost estimates for meeting future THM regulations\**

Future MCL µg/L	N	Capital Cost billion dollars	N	Operating and Maintenance Cost million dollars
50	316	1.3	268	89
25	310	1.7	268	153
5	276	8.7	240	692

\*Based on engineering study (2 percent), preliminary feasibility study (17 percent), educated guesses (57 percent), or wild guesses (23 percent)

**TABLE 6**  
*Comparison of results of national THM surveys*

Survey	Number of Cities	THMs—µg/L		
		Mean	Median	Range
NORS*†	80	68	41	ND-482
NOMS—phase 1†§	111	68	45	ND-457
NOMS—phase 2**	113	117	87	ND-784
NOMS—phase 3D††	106	53	37	ND-295
NOMS—phase 3T**	105	100	74	ND-695
NOMS—all phases	105/113	84	55	ND-784
AWWARF††‡	727	42	39	ND-360

\*NORS—National Organics Reconnaissance Survey

†Samples shipped and stored at 35–47°F (2–8°C) for one to two weeks prior to analysis

‡ND—none detected (detection levels differed significantly among the three surveys)

§NOMS—National Organic Monitoring Survey

\*\*Samples stored at 68–77°F (20–25°C) for three to six weeks prior to analysis

††Sodium thiosulfate added

‡‡Samples collected and analyzed in compliance with THM monitoring and analysis regulations

**TABLE 7**  
*Sources of supply in national THM surveys*

Source Type	Source Distribution—number (percent)		
	NORS	NOMS—Phase 2	AWWARF
Rivers, streams	38 (47)	60 (53)	137 (15)
Lakes, reservoirs	26 (33)	34 (30)	149 (16)
Ground	16 (20)	19 (17)	243 (27)
Mixed	0		254 (28)
Purchased			127 (14)
Total	80* (100)	113 (100)	910† (100)

\*Population served—36 million people

†Population served—105 million people retail; 42 million people wholesale

and completeness. Where possible, the data were processed by a personal computer using spreadsheet software.

### Results of utility survey

**Water sources and utility profiles.** Water systems serving more than 10,000 customers use a variety of sources of supply. In this analysis, the predominant source of supply was defined as that which provided at least 95 percent of a utility's water. Using the ≥95 percent criterion, the water sources were flowing streams for 15 percent of the utilities surveyed, lakes and reservoirs for 16 percent, and groundwater for 27 percent. In addition, 28 percent of the utilities received water from a mixed source of supply (usually a mixture of groundwater and surface water), and 14 percent purchased virtually all of their water. The respondents' data showed that flowing stream and lake sources were used by a somewhat disproportionate number of the larger systems; similarly, a disproportionate number of the smaller systems used groundwater. The finding that so many utilities use diverse supply sources complicates a rather simple picture previously presented by the USEPA, in which water supply sources were simply divided into three categories: flowing streams, lakes, and groundwater. The survey results also showed 11 percent of the responding utilities to be privately owned and 89 percent to be publicly held or government-owned.

Although there was a strong correlation between the size categories derived from the FRDS and AWWARF mailing lists and the size categories reported in the survey, some utilities reported serving more or fewer retail customers than the data bases indicated. Some of these differences may have resulted from respondents indicating numbers of meters or connections rather than the requested totals of people served. The median population served was 50,000, but the mean number of retail customers was 126,500. According to the respondents' data, the retail population covered by the sample was 105 million people, or about 67 percent of the 171 million people served by large water systems.

The numbers of wholesale customers served ranged from 0 to 13 million. Because there may be some overlap with retail customers, it was not feasible to add the total number of wholesale customers (42 million) to the retail customer total to provide an overall total of the population covered by this survey. Most utilities provided information on the total amount of water sold, which ranged from 1 to 480,000 mil gal (3.8 to  $1.8 \times 10^6$  ML) per year.

As a partial check of the respondents' calculations of total water sold and population served, the daily per-capita usage



was calculated. The median per-capita usage was found to be 186 gal (514 L) daily, with a mean of 286 gal (1,082 L) daily. These data are consistent with other reported data on average daily usage nationwide.<sup>2</sup>

Water cost data provided by the respondents was also viewed cautiously because many utilities cited the costs of water treatment rather than the selling price of the water. This question was obviously misunderstood by some utilities, as 10 respondents indicated that the cost of water was \$0.01 (or less)/1,000 gal. Nonetheless, the median cost reported was \$0.65/1,000 gal, and the mean was \$1.06/1,000 gal; both of these values are somewhat low but nonetheless reasonable compared with other national estimates.<sup>3</sup>

**Water treatment.** Chlorine remains the most common disinfectant among water utilities; it is used by about 85 percent of the flowing stream and lake systems and by about 80 percent of the groundwater systems. (Systems that purchase their water, however, often do not chlorinate; only about 22 percent reported that chlorine was used.) Chlorine dosages depended on the primary source of supply and the size of the system. The median was about 2.3 mg/L for flowing stream systems, 2.2 mg/L for lake systems, 1.2 mg/L for groundwater systems, and 1.0 mg/L for mixed-supply systems and water purchasers. The lowest dosage reported was 0.1 mg/L, and the highest was >20 mg/L.

Chloramines were used by about 25 percent of the flowing stream systems and the larger lake systems but by only 13 percent of the smaller lake systems. Chloramines were rarely used by groundwater systems, mixed systems, or water purchasers. Typical dosages for flowing stream systems were approximately 2.7 mg/L, compared with 1.5 mg/L for lake systems.

Relatively few other disinfectants were used by the water suppliers. Only about 10 percent of the flowing stream systems and about 5 percent of the lake and reservoir systems reported using chlorine dioxide. The lake and stream systems that used chlorine dioxide served more than 25,000 customers. The typical chlorine dioxide dosage ranged from 0.6 mg/L for the flowing stream systems to 1.0 mg/L for the lake systems. No groundwater systems used chlorine dioxide. Only one utility reported using ozone. Other oxidants were used by about 10-20 percent of the flowing stream and lake systems but by very few of the groundwater systems. Typical dosages were 0.5 mg/L for lake systems and 1.0 mg/L for groundwater systems using other oxidants. The most common "other" oxidant, by far, was potassium permanganate, although a few utilities

listed various miscellaneous chemicals, some of which were not oxidants.

A detailed discussion of the water treatment practices of survey respondents is presented in the full report on this project.<sup>3</sup>

**Purchased water.** In the sample of utilities serving 10,000 or more customers, 245 (27 percent) reported purchasing at least some of their water. This includes 12 percent of the systems supplying more than 50,000 retail customers. But only a few utilities were mentioned more than once as wholesale agencies. Among those providing water to a substantial number of utilities were the Metropolitan Water District of Southern California, the Massachusetts Water Resources Authority, and Elizabethtown Water; and the cities of San Francisco, Calif.; Detroit, Mich.; New York, N.Y.; Chicago, Ill.; Seattle, Wash.; and Cleveland, Ohio. Some utilities also reported receiving water from secondary wholesalers. For example, some Orange County and San Diego County, Calif., utilities reported their wholesaler as the Municipal Water District of Orange County and the San Diego County Water Authority, respectively, both of which are subsidiaries of Metropolitan.

**THM data.** Of the 910 responding utilities, 727 reported THM data for one or more quarterly periods, although many reported only the average (mean) quarterly readings rather than the maximum, minimum, and mean levels requested in the questionnaire. Many of the returned questionnaires from which significant data were missing came from respondents who purchased water; they stated that the wholesaler was responsible for measuring and recording THM data. Data were also missing from the surveys returned by the smaller utilities and by utilities that had misplaced their records or claimed exemptions from reporting requirements.

The THM data should be treated with some caution because all questionnaire responses marked "beneath detection level" or specifying a "less than" level were entered as 0 (zero) THMs, resulting in calculation of means that were probably somewhat lower than is actually the case.

Overall THM levels since 1984 have been steady, reflecting a relatively stable national THM picture since 1979, when the THM regulation was promulgated. Figure 1 shows that considerable quarterly fluctuations occurred over the last three years. First-quarter mean THM levels had a median of approximately 30  $\mu\text{g/L}$  for all utilities, second-quarter medians of the means were approximately 40  $\mu\text{g/L}$ , third-quarter medians were about 44  $\mu\text{g/L}$ , and fourth-quarter medians were approximately 36  $\mu\text{g/L}$  over the three-year period. This quarterly

variation may be a result of temperature effects, as higher summer water temperatures encourage the formation of high THM levels in distribution systems.

The reported THM levels vary substantially according to the water source (Figure 2). Groundwater systems have a consistently low reported median mean THM level of around 10  $\mu\text{g/L}$  but also have the highest maximum means as well as the lowest minimum means, indicating a wide range of THM levels.

With some exceptions, the data also showed that among utilities relying on river or lake sources or purchasing most of their water supply, the smaller utilities tend to have higher THM levels than the larger utilities. This unexpected result is illustrated in Table 1, which demonstrates that, except for groundwater and mixed systems, utilities in the 10,000-25,000-customer category generally had the highest THM concentrations. This finding may be because larger systems have the resources and personnel to optimize their treatment and operations so as to minimize THM concentrations.

Thirty-eight (4.6 percent) utilities reported being required to make a public notification that they had violated the 0.10-mg/L THM MCL during 1984-86, with most of those violating the regulation only once. Five utilities reported making public notifications from six to twelve times during the three-year period. Although the number of utilities reporting public notifications is consistent with data from the FRDS, it is possible that utilities that did not respond to the questionnaire were those that have had problems with THMs.

Data on other disinfection by-products—for example, DHAN, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), chloropicrin—in water utility systems were largely unavailable from the respondents. Because the USEPA has stated that it intends to regulate these other disinfection by-products, water utilities should begin developing the appropriate analytical methods and collecting the necessary data from their systems.

**Meeting the regulation.** Many US water utilities had to change their treatment methods in order to comply with the 0.10-mg/L MCL. The cost data should be interpreted cautiously, as a number of the utilities reporting changed procedures did not report capital costs for these changes. Nevertheless, the returned surveys provided a total of 268 data points on capital expenditures for the 543 reported treatment changes made to comply with the THM regulation.

Table 2 shows that the majority of the 543 treatment changes took the form of modifications to existing clarification and disinfection procedures. A large number of utilities (100) changed to

chloramines as the primary method of disinfection. The 543 treatment changes reflect more than one change per respondent, as 225 utilities reported changed treatment procedures. The distribution of treatment changes predicted in a 1981 study<sup>4</sup> closely correlates with the actual distribution determined in this study.

Tables 3 and 4 show the reported costs to the 268 and 241 utilities that provided data on the capital costs and the operating and maintenance (O&M) costs, respectively, of complying with the THM regulation. As might be expected, actual costs savings were reported by utilities that altered their disinfection practices. Extrapolating the costs reported in this survey to the total of 171 million people served by all the utilities that deliver water to more than 10,000 customers results in a range of capital costs of \$31-102 million and a range of annual O&M costs of \$8-29 million. Both ranges bracket the estimates of \$47 million capital and \$17 million O&M costs that were developed in 1981 using predicted 1985 dollars.<sup>4</sup>

**Secondary problems.** Of the 225 utilities reporting changes in treatment procedures, a significant percentage indicated that secondary problems subsequently developed. The percentages of utilities reporting problems in the areas of taste and odor, microbiological quality, corrosion, biofilm growth, and color were 39, 23, 16, 15, and 12 percent, respectively. Major problems in all categories were reported by 4 percent or less. That these types of secondary problems should accompany any change in treatment technology is not surprising, but they were unanticipated by many utilities.

**Lowering the MCL.** Survey respondents were asked (1) to estimate the capital and O&M costs of lowering the THM regulation to three different levels and (2) to indicate what methods would likely be used to meet those standards. In addition, they were asked to indicate the basis for their estimates and to give an opinion on the need for lower THM standards. Table 5 indicates that billions of dollars in capital costs and hundreds of millions of dollars in O&M costs can be expected to be incurred in meeting future regulations. Several dozen procedures were anticipated by the utilities to meet future THM regulations, including treatment processes such as ozone or granular activated carbon.

Responses to the questions about lowering the MCL were not completed by all the utilities surveyed, nor did they represent firm estimates rooted in detailed engineering studies; rather, the responses received were largely educated guesses about the costs of meeting lowered standards. The relatively low response (about 30 percent) to the cost

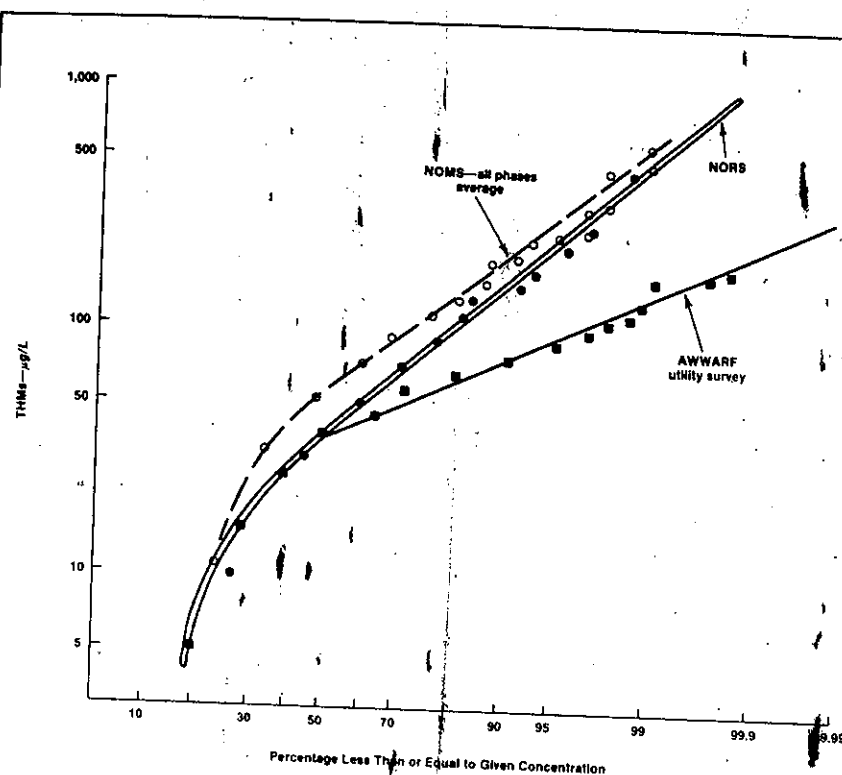


Figure 3. Frequency distributions of national THM survey data

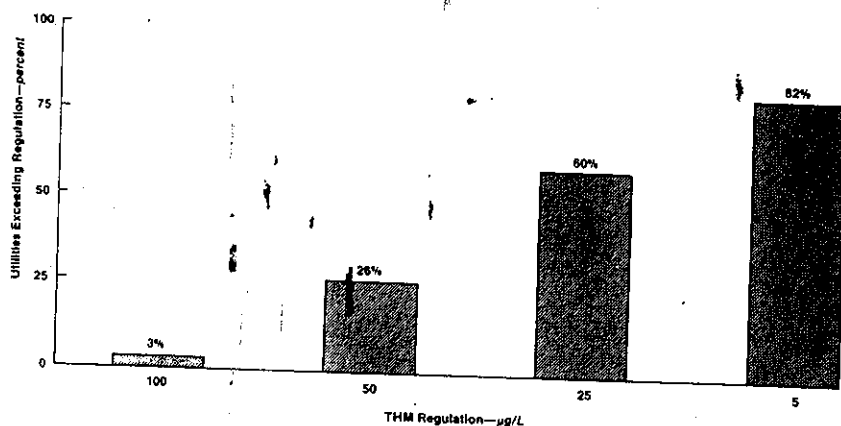


Figure 4. Predicted compliance with stricter regulation (based on 12 quarters of mean THM data)

estimate section of the questionnaire suggests that many water quality managers (and presumably government regulators) have no realistic idea of the costs to be expected. Fifty-seven percent of the respondents indicated that their estimate was an "educated" guess; 23 percent called it a "wild" guess. Only 17 percent had prepared a preliminary feasibility study, and only 2 percent had done a detailed engineering study. Clearly, further detailed analysis would be required to develop firm cost data.

Water quality managers completing the questionnaire were generally (about 75 percent) opposed to lowering the MCL, indicating that they believed that there

was no health risk and that the costs were not worth the benefits. The USEPA estimates of the toxicity of THMs were generally considered erroneous, and lowering the MCL was seen as an over-reaction to questionable data.

Approximately 18 percent favored lowering the MCL to technically feasible levels because of expected health benefits. The remaining 7 percent provided neutral answers, usually stating that more study was needed.

**Survey comparisons.** Table 6 compares the AWWARF survey results with those of two previous surveys by the USEPA: the National Organics Reconnaissance Survey (NORS) in 1975 and the National

**TABLE 8**  
*THM monitoring required by states for utilities serving fewer than 10,000 people*

State	Monitoring Conditions
Michigan	State monitors surface water supplies as well as those utilities at which there is a specific reason to believe THM levels are greater than 0.10 mg/L.
New Hampshire	State monitors all systems on an irregular schedule.
New York	State monitors surface water supplies only. Frequency is one sample per quarter per system and can be reduced if running annual average is less than 75 µg/L.
Rhode Island	State monitors, on a quarterly basis, all systems that disinfect.

**TABLE 9**  
*Results of AWWARF state THM survey*

Parameter	State Survey	US Total
Number of utilities serving <10,000 people	677	55,449
Population served—million	1.6	48
Number of states	12	50

**TABLE 10**  
*THM data for utilities serving fewer than 10,000 people*

State	Number of Cities	Population	Number of Data Points	THMs—µg/L	
				Mean	Range
Alaska	81	24,304	119	21	ND*-184
Illinois	57	185,363	57	56	9-184
Iowa	17	44,584	65	155	ND-292
Maryland	12	48,204	126	29	2-104
Michigan	14	78,454	408	78	23-189
Montana	9	32,801	60	22	ND-34
New York	236	609,500	900	49	4-308
Pennsylvania	8	24,438	15	32	4-63
Rhode Island	11	38,012	11	41	ND-115
South Carolina	20	54,445	632	107	34-313
West Virginia	8	41,048	48	53	33-80
Wisconsin	204	435,035	204	2	ND-42
Total	677	1,616,188	2,594	†	ND-313

\*ND—none detected

†Mean—36; median—18

utilities could not meet an MCL of 50 µg/L. Similarly, 60 and 82 percent of the utilities could not meet MCLs of 25 and 5 µg/L, respectively. The full report<sup>3</sup> shows how the percentage of utilities failing a stricter THM regulation would rise if quarterly maximum THM data were used. The value of 3 percent for utilities failing to meet a 0.10-mg/L MCL compares favorably with the number of utilities reporting a previous public notification (38 utilities, or 4.6 percent of the total of 821 utilities that responded to this question).

### Results of state survey

Only four states (Michigan, New Hampshire, New York, and Rhode Island) require that utilities serving fewer than 10,000 customers monitor for THMs or that the states do the monitoring (Table 8). Only New York requires smaller utilities to comply with a 0.10-mg/L MCL. Twenty-four states responded that THM data were available for the smaller utilities, but Table 9 shows that usable data were received from only 12 states. Table 9 also shows that the number of utilities (677) for which THM data were received represents only a small percentage of the total number serving fewer than 10,000 customers.

Table 10 summarizes 2,594 THM data points for the 12 states reporting usable data for the smaller utilities. Some of these data come from special studies of small systems.<sup>8,9</sup> The low THM results from Wisconsin, with 204 cities sampled, appear to affect the overall statistics markedly. Figure 5 shows that the data from Table 10 are not representative of the NORS and NOMS data, nor are these data representative of the AWWARF utility survey data in Figure 3. This lack of agreement may be a result of nonrepresentative data in this survey or the possibility that smaller systems use sources that are generally lower in THM precursors. Removing the Wisconsin data improves agreement with NORS and NOMS, but significant differences still exist. More THM data on smaller utilities are needed to construct a representative picture of how a more restrictive, more widely applicable THM regulation would affect those utilities.

### Summary and conclusions

- The AWWARF THM survey was designed and executed to obtain representative data on compliance with the THM regulation. A very high percentage (73 percent) of the questionnaires was returned. When both the retail and wholesale populations served by the questionnaire respondents are taken into consideration, more than 67 percent of the population represented by water utilities serving more than 10,000 customers is reflected in the survey results.

Organic Monitoring Survey (NOMS) in 1976-77.<sup>5-7</sup> Comparing the AWWARF overall THM average of 42 µg/L with the averages of the NORS and NOMS (all phases) shows a 40-50 percent reduction in national THM concentrations as a result of compliance with the THM regulation.

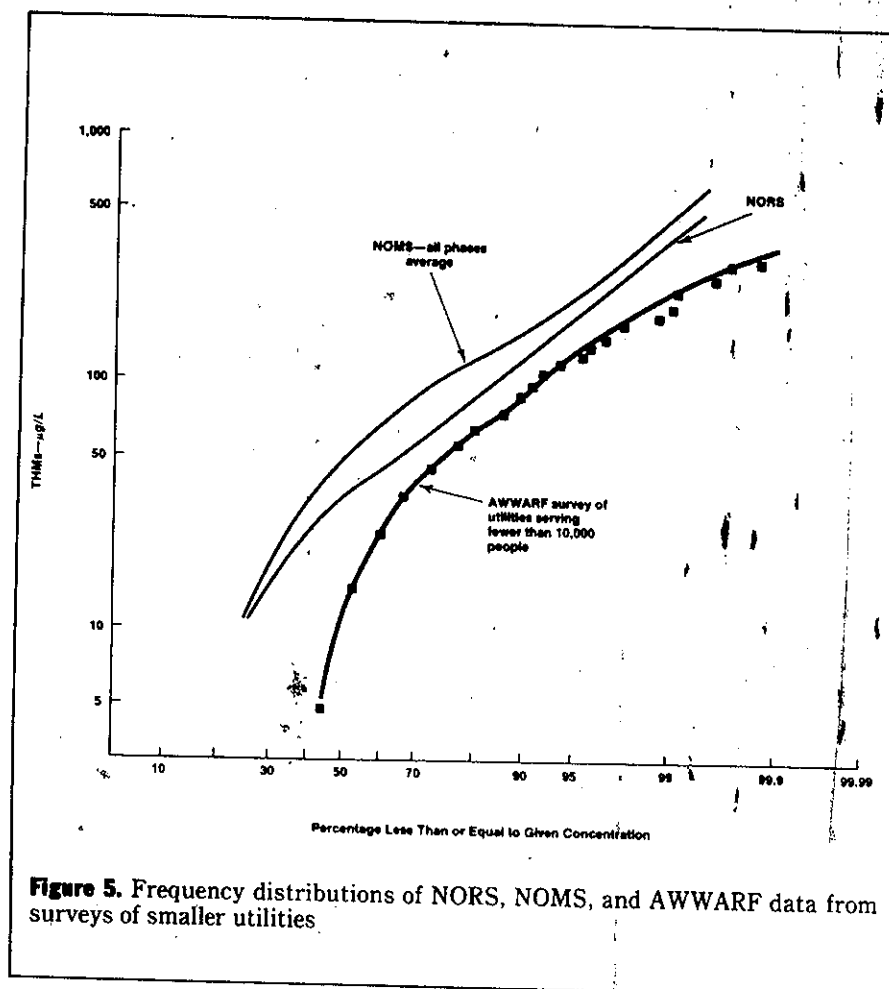
Table 7 compares the sources of supply for the NORS, NOMS, and AWWARF THM surveys. Overall, the NORS and NOMS sources were very similar. The AWWARF distribution of source types more clearly reflects the variety of sources actually in use in the United States. The THM data compared in Figure 2 indicate that the "mixed-source"

and "purchased" categories appear, with respect to THMs, similar to the "surface supplies" category. In general, there are no substantial differences among the surveys that would cause problems in comparing their THM data.

Figure 3 is a log-log frequency distribution graph of the THM data represented in Table 6. For utilities with THMs of 50 µg/L and lower, the occurrence of THMs is about the same for all three surveys. Compliance with the THM regulation, however, has clearly reduced the higher concentrations of THMs found by NORS and NOMS.

Figure 4, which was derived from Figure 3, indicates that 26 percent of the





**Figure 5.** Frequency distributions of NORS, NOMS, and AWWARF data from surveys of smaller utilities

- On the average, enactment of the THM regulation resulted in a 40-50 percent reduction in the concentrations of THMs in larger utility systems. Thirty-eight, or about 4.6 percent, of the responding utilities exceeded the MCL at least once during the period 1984-86.

- Compliance with the 0.10-mg/L THM regulation resulted in estimated capital expenditures of \$31-102 million and yearly O&M costs of \$8-29 million.

- The quality of the questionnaire responses was highly variable. Only 29 percent of the questionnaires could be processed without some type of special handling. A review of the questionnaires showed that a significant number of key employees of water utilities had little understanding of water quality issues in general or of THMs in particular.

- Some 75 percent of the water quality managers believed USEPA should not lower the MCL below 0.10 mg/L.

- Although compliance with the 0.10-mg/L MCL was not particularly costly for water utilities, lowering the MCL significantly below 50 µg/L would cause massive numbers of utilities to exceed the MCL and would require billions of dollars of capital expenditures to bring those utilities into compliance.

- The preceding conclusions, coupled with the lack of understanding of the

issues demonstrated by water utility personnel, suggest that the USEPA will have a difficult time eliciting compliance with a new, significantly more stringent THM regulation.

- Because the cost data obtained are so uncertain, a detailed economic impact analysis is needed to determine the expected costs to water utilities of compliance with a stricter THM regulation.

- Only four states require that smaller utilities monitor for THMs. The limited THM data gathered from state records indicate that these data for small systems are not consistent with pre-THM-regulation data (NORS and NOMS) for larger utilities. Not enough data were available to determine whether this lack of consistency was caused by nonrepresentative data in the sample used or by the possibility that smaller systems use water sources that are generally lower in THM precursors, i.e., groundwater.

- More data are needed before THM concentrations for smaller US utilities can be determined. Only then will it be possible to determine the potential impacts of a stricter, more widely applicable THM regulation.

#### Acknowledgment

This work was partially supported by a grant from the AWWARF; special

thanks are extended to Jon DeBoer for his guidance and assistance. Many people at Metropolitan, the USEPA, AWWA, the Association of State Drinking Water Administrators, and individual state regulatory agencies assisted with this project, and their help is appreciated. Special thanks are extended to the personnel of the 910 water utilities who took time to fill out the questionnaires that served as the basis for this study.

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## RESEARCH &amp; TECHNOLOGY

# The Occurrence of Disinfection By-products in US Drinking Water

Stuart W. Krasner, Michael J. McGuire, Joseph G. Jacangelo, Nancy L. Patania, Kevin M. Reagan, and E. Marco Aieta



PHOTOS BY RICHARD RAVENSTINE

Data were gathered on the presence of disinfection by-products (DBPs) in drinking water and on the impact of treatment processes on DBP formation and control. Thirty-five water treatment facilities were selected to provide a broad range of source water qualities and treatment processes. Trihalomethanes were the largest class of DBPs detected (on a weight basis) in this study, with haloacetic acids being the next most significant DBP fraction. Formaldehyde and acetaldehyde, by-products of ozonation, were also demonstrated to be produced by chlorination. Cyanogen chloride was found to be preferentially produced in chloraminated water.

The US Environmental Protection Agency (USEPA) will be developing regulations to control disinfection by-products (DBPs) as a result of the 1986 amendments to the Safe Drinking Water Act (SDWA). Under these amendments, the USEPA is required to develop a priority list of chemicals that may be present in drinking water. Included on the list are trihalomethanes (THMs) and other DBPs. If the provisions of the SDWA are to be met by the beginning of 1991, the presence and control of these DBPs must be fully understood. In September 1987, the USEPA's Office of Drinking Water entered into a cooperative agreement with the Association of Metropolitan Water Agencies (AMWA) to perform a study of the occurrence and control of DBPs. The AMWA contracted with the Metropolitan Water District of Southern California (MWD) to provide management services for the project and to perform the DBP analyses. Metropolitan subcontracted with James M. Montgomery Consulting Engineers Inc. to provide engineering services and some analyses for the study. In addition, the State of California Department of Health Services (CDHS), through the California Public Health Foundation (CPHF), contracted with MWD and James M. Montgomery to perform a similar study in California.

The USEPA study included 25 water utilities across the United States, and the CDHS study involved 10 water utilities in California. During the first year

of this project, baseline data were gathered on all 35 water utilities. The DBPs under investigation included THMs; haloacetonitriles (HANs); halo ketones (HKs); haloacetic acids (HAAs); chloro-

picrin (CHP); chloral hydrate (CH); cyanogen chloride (CNCl); 2,4,6-trichlorophenol; formaldehyde; and acetaldehyde (Figure 1). This article focuses on some of the significant preliminary findings of these DBP studies.

## Experimental procedures

The sampling and analytical procedures utilized in these studies are described in detail elsewhere. Grab samples (Table 1) were collected at clearwell effluents (after final disinfection but prior to distribution). Total organic car-

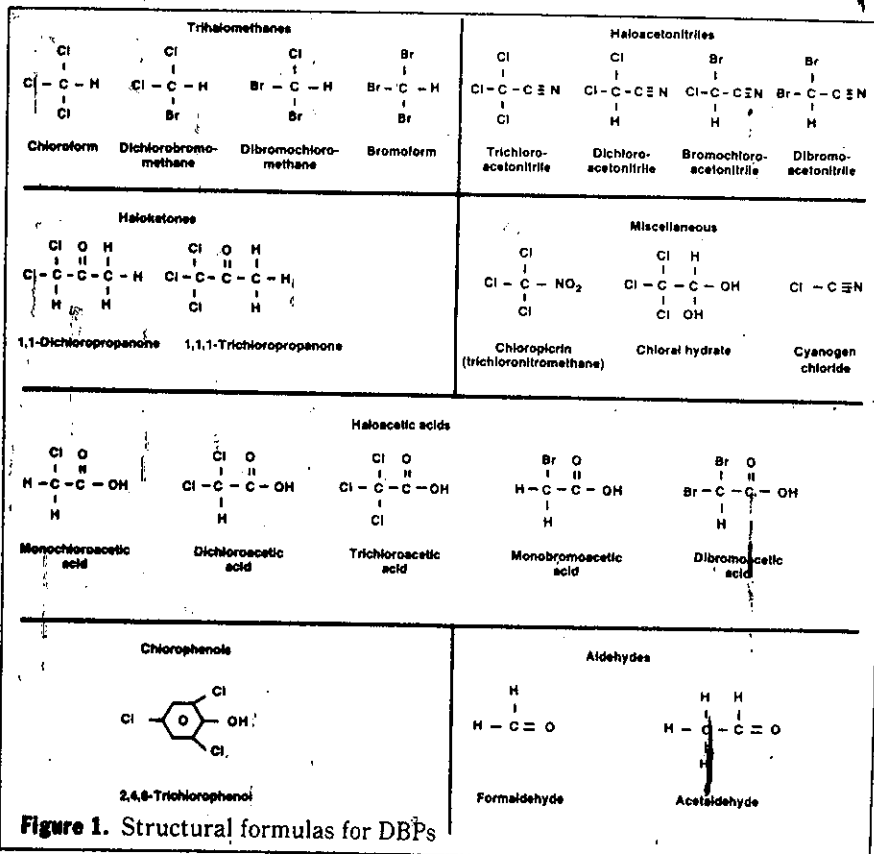


Figure 1. Structural formulas for DBPs

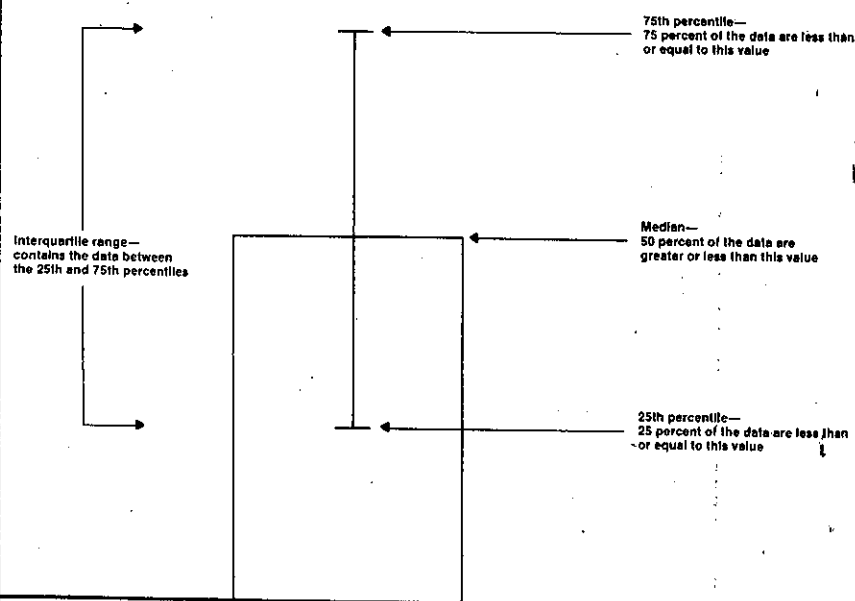
**TABLE 1**  
*Contents of sampling kit*

Analytical Fraction	Number and Size of Sample Bottles	Dechlorination Agent or Preservative*
Plant influent sample bottles		
Formaldehyde/acetaldehyde	3, 40 mL	None; HgCl <sub>2</sub> solution + NH <sub>4</sub> Cl crystals†
Bromide/chloride	1, 60 mL	None
TOC/UV	3, 60 mL	None*
Filter influent sample bottles		
TOC/UV	3, 60 mL	None*
Clearwell effluent sample bottles		
PE-DBPs‡	3, 40 mL	65 mg NH <sub>4</sub> Cl crystals
CH	3, 40 mL	20 mg ascorbic acid
HAAs§	4, 40 mL	65 mg NH <sub>4</sub> Cl crystals
CNCl	4, 40 mL	20 mg ascorbic acid
Formaldehyde/acetaldehyde	3, 40 mL	None; HgCl <sub>2</sub> solution + NH <sub>4</sub> Cl crystals†
TOX	2, 250 mL	None*
TOC/UV	3, 60 mL	None*
Additional bottles in kit		
Travel blank—NH <sub>4</sub> Cl	2, 40 mL	65 mg NH <sub>4</sub> Cl crystals
Travel blank—ascorbic acid	2, 40 mL	20 mg ascorbic acid
Travel blank—formaldehyde	2, 40 mL	None; HgCl <sub>2</sub> solution + NH <sub>4</sub> Cl crystals†

\*For the following analytical fractions, additional reagents were added after sampling as soon as possible after receipt at MWD: TOC/UV—acidify with reagent-grade phosphoric acid to pH < 2; TOX—dechlorinate and acidify, respectively, by adding 0.5 mL of 50 percent sulfuric acid and three drops (utilizing a 3.5-in. pasteur pipette) of a fresh saturated sodium sulfite solution. †No dechlorination agent and preservative were used during second and third sampling quarters; 40 µL of a 10-mg/mL mercuric chloride solution plus 65 mg ammonium chloride crystals were used during fourth sampling quarter. ‡PE-DBPs (pentane-extractable disinfection by-products) are THMs, HANs, HKs, and CHP. §Includes 2,4,6-trichlorophenol

**TABLE 2**  
*Sample holding times*

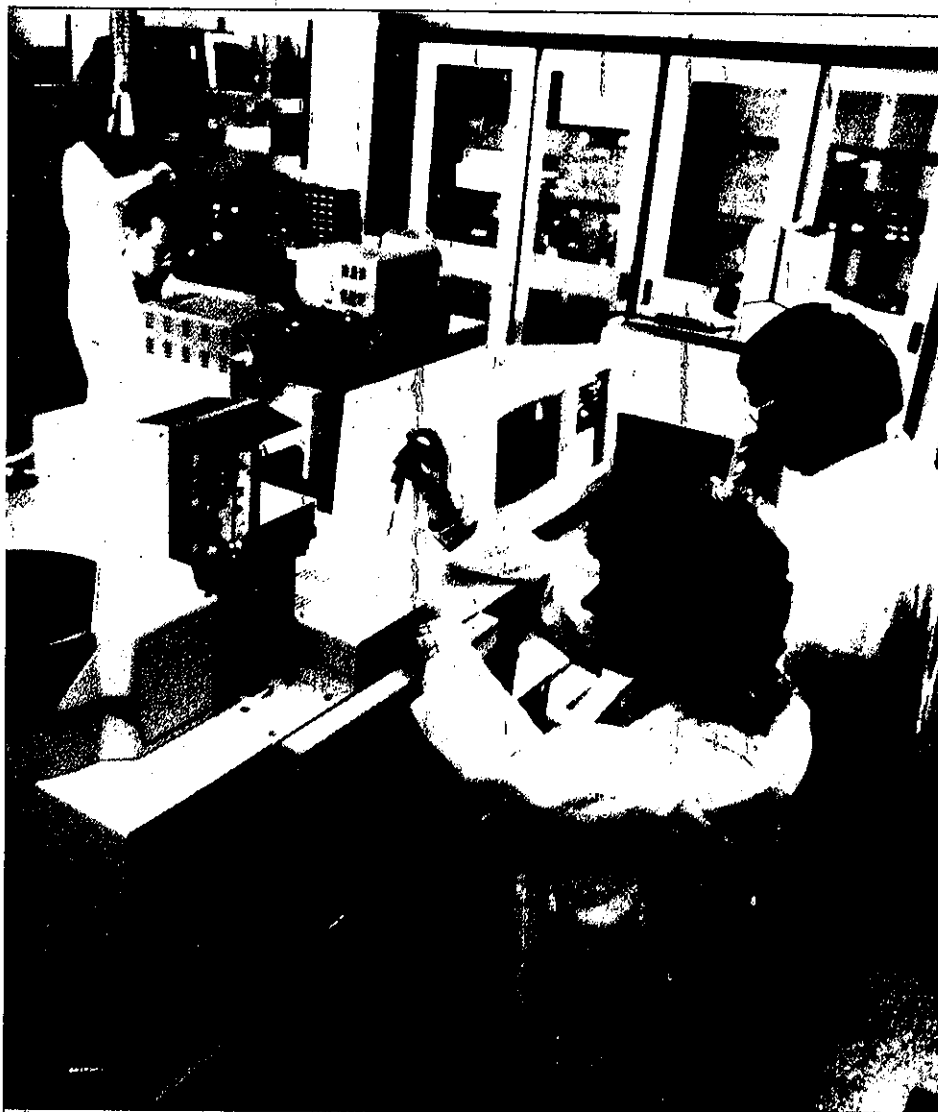
Analytical Fraction	Sample Holding Limit	Extract Holding Limit
PE-DBPs	Extract immediately	2 weeks
CH	21 days	15 days
HAAs	9 days	7 days
CNCl	Analyze immediately	Not applicable
Formaldehyde/acetaldehyde	Extract immediately	
TOX	2 weeks	Not applicable
TOC/UV	28 days	Not applicable
Bromide/chloride	28 days	Not applicable



**Figure 2.** Guide to bar chart presentation using median and percentiles

Gas chromatography was used by chemists at MWD for the analysis of disinfection by-products, including trihalomethanes, haloacetonitriles, haloacetones, haloacetic acids, chloropicrin, chloral hydrate, cyanogen chloride, formaldehyde, acetaldehyde, and 2,4,6-trichlorophenol.

bon (TOC) analyses of the plant influent and filter influent were performed, starting with the second sampling quarter. Also starting with that quarter, ultraviolet (UV) absorbance was measured at all three sampling points, the bromide and chloride levels of plant influents were determined, and formaldehyde and acetaldehyde analyses were made of the clearwell effluents. Some plant influents were analyzed for these aldehydes during the third sampling quarter; all plant influents were analyzed for aldehydes during the fourth sampling quarter. Samples were dechlorinated, preserved (Table 1), and analyzed as soon as possible within established holding times (Table 2). The dechlorination agents and preservatives for the DBP fractions were evaluated in holding studies to ensure that analyte concen-

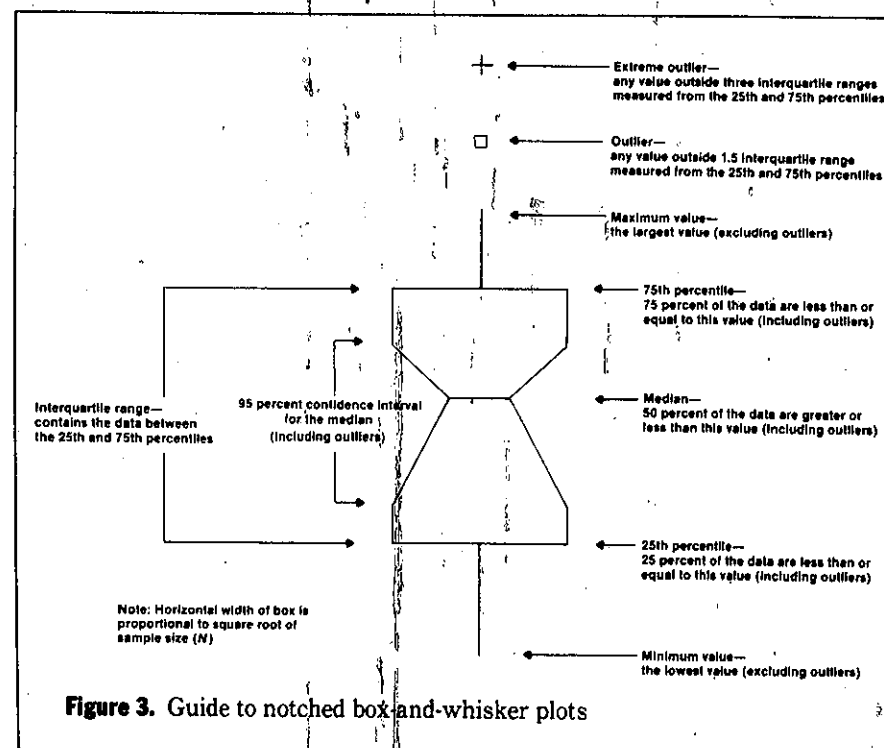


trations held to  $\pm 20$  percent of their initial values. Total organic halide (TOX) samples were dechlorinated with a sodium sulfite solution. Because sampling kits were prepared and shipped to field locations at least two weeks prior to sampling, the instability of the dechlorination solution required that TOX samples be dechlorinated and preserved upon receipt at the laboratory.

A method that employed modified THM liquid-liquid extraction (LLE) was developed for the analysis of THMs, HANs, HKs, and CHP.<sup>2</sup> For this analytical fraction, pentane was used as the extraction solvent, sodium sulfate was added to improve the partitioning from the aqueous phase to the solvent, and a capillary gas chromatograph-electron capture detector (GC-ECD) was utilized for adequate resolution of the analytes. The more polar chloral hydrate required a similar LLE method, but methyl *t*-butyl ether was used as the extraction solvent.<sup>3</sup> Haloacetic acids and 2,4,6-trichlorophenol were analyzed by an acidic, salted ether LLE, and they required esterification with diazomethane prior to GC-ECD analysis.<sup>3</sup> CNCl was analyzed by a purge-and-trap gas chromatograph-mass spectrometer (GC-MS) method.<sup>3</sup>

Formaldehyde and acetaldehyde were analyzed by a derivatization-extraction GC-ECD method.<sup>4</sup> First, 20 mL of sample was transferred into a 30-mL vial. Then 1 mL of a freshly prepared 2 mg/mL solution of *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBOA)\* was added to each sample and swirled. After being held for 2 h ( $\pm 5$  min), each sample was quenched by adding 0.05 mL of concentrated sulfuric acid and swirling. The sample was extracted with 4 mL of pentane, shaken for 5 min, and then allowed to stand for 5 min to separate the layers. The pentane extract was transferred to two 1.5-mL vials and stored at 4°C until it was ready for GC analysis (Table 3).

After receipt of the samples at Metropolitan's laboratory, the TOC samples were acidified with reagent-grade phosphoric acid to a pH of  $< 2$ . This preservation technique was also used on the UV samples. UV absorbance was measured at 254 nm with a UV-visible spectrophotometer\* and a 1-cm quartz cell. The UV was also measured at 800 nm to provide a correction for the presence of turbidity or suspended solids. Because some plant effluent samples were chloraminated, monochloramine—which has UV absorbance at 243 nm—could have presented an interference problem. However, the acid preservation converted monochloramine to dichloramine in approximately 2 h. The latter species has a UV peak at 293 nm, so it did not present



**Figure 3.** Guide to notched box-and-whisker plots

\*Aldrich Chemical Co. Inc., Milwaukee, Wis.

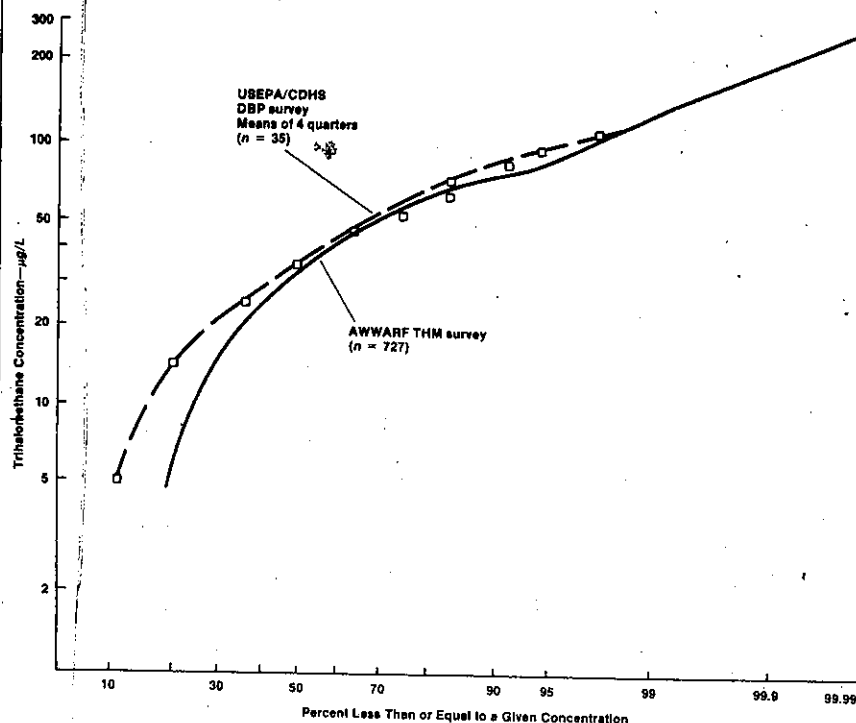
**TABLE 3**  
*Gas chromatograph\* parameters for formaldehyde and acetaldehyde*

Parameter	Value
Sample size	2 $\mu$ L
Injector	150°C; splitless; split open at 0.5 min
GC column	Durabond-5† fused silica capillary; 30-m $\times$ 0.25-mm ID; 1.0- $\mu$ m film thickness
Column temperature program	50°C, 1.0 min $\rightarrow$ 8°C/min $\rightarrow$ 122°C, 7 min $\rightarrow$ 30°C/min $\rightarrow$ 245°C, 2 min
Column carrier gas	Helium at 1.5 mL/min; measured at 25°C
Detector	Electron capture with Ni-63 at 272°C
Detector makeup flow	Nitrogen at 24 mL/min
Autosampler‡ parameters	
Purge pulse pressure	55 psi
Number of purge pulses	1

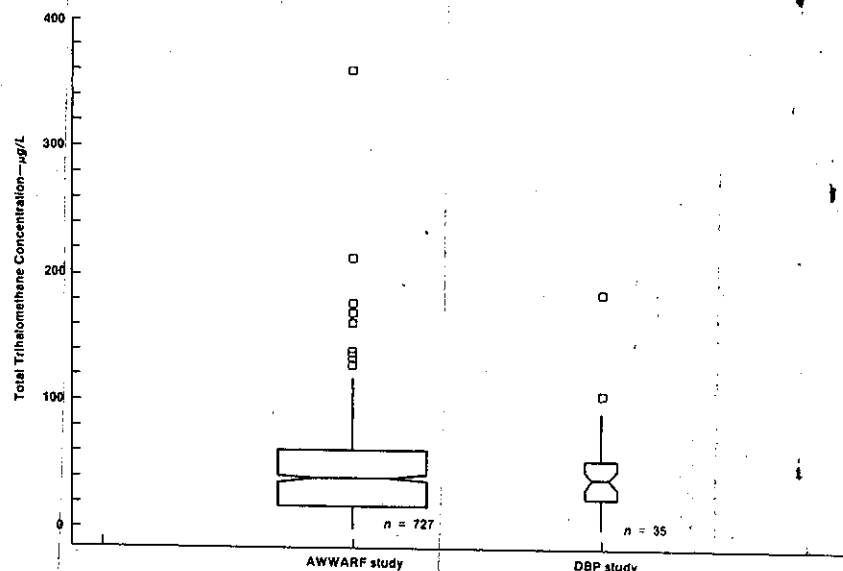
\*Models 3400 and 3500, Varian Instrument Group, Sunnyvale, Calif.

†J&W Scientific, Folsom, Calif.

‡Model 8035, Varian, Los Altos, Calif.



**Figure 4.** Frequency distributions of THM survey data



**Figure 5.** Notched box-and-whisker plot of TTHMs for AWWARF survey (12 quarters) and DBP study (4 quarters)

an interference problem. To evaluate the effect of the phosphoric acid on the UV results, some parallel unpreserved effluent samples were also analyzed; these yielded results comparable to those of the acidified samples.

Bromide and chloride were analyzed with an ion chromatograph,† a 20- or 50- $\mu$ L sample loop, a high-performance ion chromatography analytical column,‡ an anion micromembrane suppressor, and a conductivity detector. The eluant was a solution of 2 mM  $\text{Na}_2\text{CO}_3$  and 1 mM  $\text{NaHCO}_3$ .

## Results and discussion

**Statistical analysis.** The data from these studies were evaluated based on a comparison of parametric and nonparametric analyses. Parametric analyses assume a statistical distribution of data (e.g., Gaussian), whereas nonparametric analyses do not. In parametric analyses, an arithmetic mean or average value can be calculated for a set of data that follows a normal distribution. However, if the data include levels of compounds that are too low to be measured precisely, such results are often reported as "not detected" (ND). Unfortunately, statistical handling of the NDs, e.g., setting at zero or the minimum reporting level (MRL), can generate misleading information.<sup>5</sup> However, in nonparametric analyses, a median can be calculated so that there is an even number of observations above and below it, regardless of the presence of ND values. Also, because DBP classes and individual DBPs were found to represent a variety of statistical distributions, the presentation of data for this article and for the study is based on nonparametric analyses.

Figure 2 provides a guide to the manner in which the nonparametric analyses are presented. For most data presented here, medians and upper and lower quartiles were employed. The median represents the value above or below which 50 percent of the data are found. The 75th and 25th percentiles represent the values below which 75 and 25 percent, respectively, of the data are found.

For the presentation and interpretation of some of the data, another nonparametric analysis was employed. The results are presented by means of notched box-and-whisker plots (Figure 3).<sup>6</sup> This type of presentation conveys to the reader much more information than the simplified median and quartile presentation discussed previously. In addition to medians and percentiles, minimum, maximum, and outlier values are shown. Also, the 95 percent confidence interval for the median and an indication of the sample size are given. It should be noted that the calculations for the medians, quartiles, and 95 percent confidence interval included outlier values.

**Utility selection.** To ensure that the



results of these studies, as well as the DBP control measures practiced by the selected utilities, were representative, a matrix for utility selection was constructed based on four parameters: (1) type of source water (lake-reservoir, flowing stream, or groundwater); (2) treatment type (conventional, direct filtration, softening, or disinfection only); (3) three-year average THM level ( $<25$ ,  $25-50$ , or  $>50$   $\mu\text{g/L}$ );<sup>7</sup> and (4) population ( $\leq 50,000$  or  $>50,000$ ). An attempt was made to include at least one utility in each category of the matrix. Consideration was also given to geographic location (to include a nationwide representation) and the type of disinfectant or disinfectants in use (free chlorine, chloramines, chlorine dioxide, or ozone).

Baseline analyses were performed on a quarterly basis for the spring, summer, and fall of 1988 and the winter of 1989. The median total THM (TTHM) values for these four quarters were 34, 44, 40, and 30  $\mu\text{g/L}$ , respectively. These data were compared with the THM values obtained in a survey of 727 utilities nationwide conducted for the AWWA Research Foundation (AWWARF) in 1987.<sup>7</sup> The median TTHM concentrations in the AWWARF survey for the spring, summer, fall, and winter seasons were 40, 44, 36, and 30  $\mu\text{g/L}$ , respectively. (The AWWARF survey reflected more than 67 percent of the population represented by water utilities serving more than 10,000 customers.)

Because of the similarity of TTHM levels for the DBP studies and the AWWARF survey, the data were evaluated further. The THM regulation examines the running annual average for each utility;<sup>8</sup> therefore, mean values were computed for each of the 35 utilities for the four sampling quarters. The AWWARF survey utilized the means of three years of quarterly data. The means for both projects are plotted on a frequency distribution curve (Figure 4). (A log scale was used for the ordinate axis to compress the displayed range, not to imply a lognormal distribution.) Visually, the 35-utility DBP study appears to represent a THM frequency distribution similar to that of the 727-utility AWWARF survey. The major difference is in the data for low THM levels ( $\leq 25$   $\mu\text{g/L}$ ). The DBP study attempted to achieve a balance among utilities with low, medium, and high THM levels. The resulting limitation on the number of utilities with very low THM levels may have been responsible for the difference between the data below 25  $\mu\text{g/L}$  TTHMs for the two surveys. A statistical comparison of the two distributions, by means of a Kolmogorov-Smirnov test,<sup>9</sup> indicates that the hypothesis that these



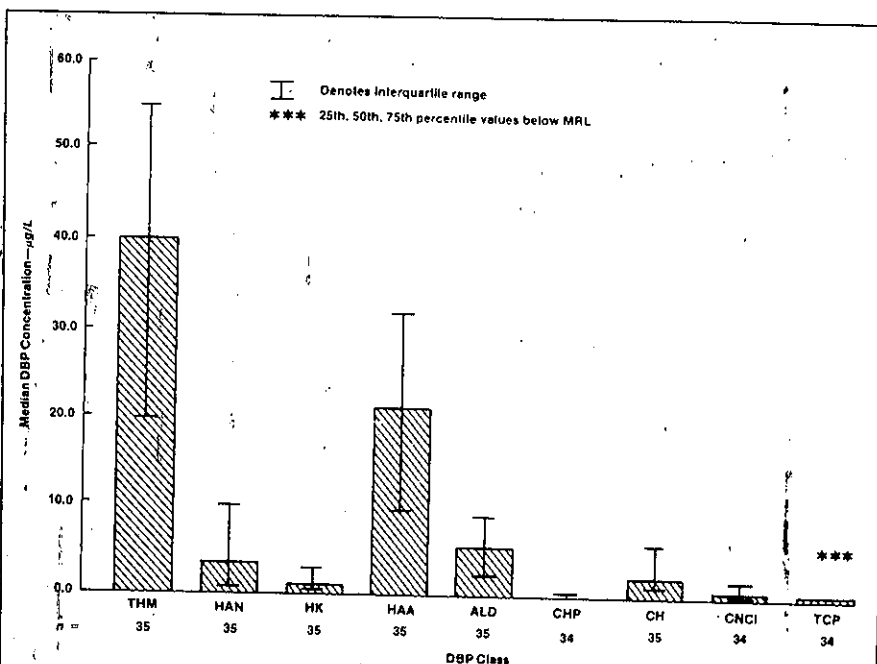
Beginning with the second sampling quarter, total organic carbon analyses of the plant influent and filter effluent were performed.

samples are from the same distribution is not rejected at a significance level of 0.01.

In addition, a notched box-and-whisker plot of TTHMs for the two surveys was evaluated (Figure 5). Both sets of survey results have median TTHM values of 39  $\mu\text{g/L}$ , and the 95 percent confidence intervals for the medians overlap, indicating that the two groups are statistically similar in terms of cen-

tral tendency. Furthermore, their minimums and maximums are comparable, indicating a similarity in variability.

**Baseline results.** Table 4 shows baseline data for the four sampling quarters. As would be expected based on seasonal temperature differences, the highest THM levels are in the summer and the next highest in the fall. For many utilities in California and the South, fall can be almost as warm as summer. For the



**Figure 6.** DBP concentration by class for third quarter (THM—trihalomethanes; HAN—haloacetonitriles; HK—haloketones; HAA—haloacetic acids; ALD—aldehydes; CHP—chloropicrin; CH—chloral hydrate; CNCl—cyanogen chloride; TCP—2,4,6-trichlorophenol)

<sup>7</sup>Lambda 5, Perkin-Elmer Corp., Norwalk, Conn.  
<sup>8</sup>Model 2000, Dionex Corp., Sunnyvale, Calif.  
<sup>9</sup>AS4A, Dionex Corp., Sunnyvale, Calif.

**TABLE 4**  
Quarterly median values of DBPs in drinking water

Disinfection By-product	Concentration— $\mu\text{g/L}^*$			
	1st Quarter (Spring 1988)	2nd Quarter (Summer 1988)	3rd Quarter (Fall 1988)	4th Quarter (Winter 1989)
Trihalomethanes				
Chloroform	15	15	13	9.6
Bromodichloromethane	6.9	10	5.5	4.1
Dibromochloromethane	2.6	4.5	3.8	2.7
Bromoform	0.33	0.57	0.88	0.51
Total trihalomethanes†	34	44	40	30
Haloacetonitriles				
Trichloroacetonitrile	<0.012	<0.012	<0.029	<0.029
Dichloroacetonitrile	1.2	1.1	1.1	1.2
Bromochloroacetonitrile	0.50	0.58	0.70	0.59
Dibromoacetonitrile	0.54	0.48	0.51	0.46
Total haloacetonitriles	2.8	2.5	3.5	4.0
Haloketones				
1,1-Dichloropropanone	0.52	0.46	0.52	0.55
1,1,1-Trichloropropanone	0.80	0.35	0.60	0.66
Total haloketones	1.4	0.94	1.0	1.8
Haloacids				
Monochloroacetic acid	<1.0	1.2	<1.0	1.2
Dichloroacetic acid	7.3	6.8	6.4	5.0
Trichloroacetic acid	5.8	5.8	6.0	4.0
Monobromoacetic acid	<0.5	<0.5	<0.5	<0.5
Dibromoacetic acid	0.9	1.5	1.4	1.0
Total haloacids	18	20	21	13
Aldehydes				
Formaldehyde	NA‡	5.1	3.5	2.0
Acetaldehyde	NA	2.7	2.6	1.8
Total aldehydes	NA	6.9	5.5	4.2
Miscellaneous				
Chloropicrin	0.16	0.12	0.10	0.10
Chloral hydrate	1.8	3.0	2.2	1.7
Cyanogen chloride	0.45	0.60	0.65	0.80
2,4,6-Trichlorophenol	<0.3	<0.4	<0.4	<0.4
Halogenated DBP <sub>sum</sub> §	64	82	72	58
Total organic halide	150	180	170	175
Plant influent characteristics				
Total organic carbon— $\text{mg/L}$	NA	2.9	2.9	3.2
Ultraviolet absorbance— $\text{cm}^{-1}$	NA	0.11	0.11	0.13
Chloride— $\text{mg/L}$	NA	28	32	23
Bromide— $\text{mg/L}$	NA	0.07	0.10	0.07

\*Except where otherwise indicated (plant influent characteristics)

†Total class median values are not the sums of the medians of the individual compounds but rather the medians of the sums of the compounds within that class.

‡NA—not analyzed

§The halogenated DBP<sub>sum</sub> median values are not the sum of the class medians for all utilities but rather the medians of the halogenated DBP<sub>sum</sub> values for all utilities. This value is only the sum of XDBPs measured in this study.

**TABLE 5**  
DBP concentrations at utility with highest bromide level (utility 10)\*

Component	Summer 1988	Fall 1988	Winter 1989
Plant influent— $\text{mg/L}$			
Total organic carbon	4.6	4.9	5.3
Chloride	640	561	680
Bromide	3.0	2.9	2.8
Clearwell effluent— $\mu\text{g/L}$			
Chloroform	0.95	0.59	0.72
Bromodichloromethane	3.8	2.9	4.1
Dibromochloromethane	8.6	9.2	11
Bromoform	30	40	31
Total trihalomethanes	43	53	47
Trichloroacetonitrile	<0.012	<0.029	<0.029
Dichloroacetonitrile	0.34	0.24	0.27
Bromochloroacetonitrile	1.2	1.1	1.1
Dibromoacetonitrile	5.9	6.7	6.0
Total haloacetonitriles	7.4	8.0	7.4
Monochloroacetic acid	<1.0	<1.0	1.0
Dichloroacetic acid	0.9	0.8	0.9
Trichloroacetic acid	<0.6	<0.6	<0.6
Monobromoacetic acid	1.2	1.2	1.4
Dibromoacetic acid	19	13	7.8
Total haloacetic acids	21	15	11

\*Data for spring 1988 were not included because bromide was not measured that quarter.

35 utilities, chloroform is the THM with the highest median; the more brominated THMs have the lowest medians. A total class median value was not the sum of the medians of individual compounds, but rather the median value of the sum of all the compounds within that class. To illustrate, the median for a compound (chloroform, for example) during a quarterly monitoring period was the median of the 35 measured values of chloroform for that quarter. For each utility, the sum of the individual compounds within a class was computed, and then the median of these 35 sums was determined. Finally, the sum of the individual halogenated DBP compounds measured in this study (i.e., XDBP<sub>sum</sub>) was computed, and then the median of these 35 sums was determined.

Further examination of the data for the third sampling quarter (Figure 6) shows that, on a weight basis, THMs were the largest class of DBPs detected in this study. The second largest fraction was the HAAs. The median level of THMs was approximately twice that of HAAs. For the four quarters of baseline sampling, an annual average of the sum of HAAs was computed for each of the 35 utilities. The median value of these running annual averages was  $19\mu\text{g/L}$ . In other research on the aqueous chlorination of humic and fulvic acids, dichloro- and trichloroacetic acid (DCAA and TCAA) have been determined to be major chlorination by-products.<sup>10-13</sup> The third largest fraction detected was the aldehydes. Although these low-molecular-weight aldehydes were initially discovered as by-products of ozonation,<sup>4,14</sup> they also appear to be by-products of chlorination. The trends shown in Figure 6 for the third quarter were also observed in the other sampling quarters.

During the first quarter of baseline sampling, correlation matrixes based on linear regression analyses were conducted to identify any obvious relationships between the various water quality parameters and the DBPs or between the DBPs themselves. There was a good correlation between HANs and THMs: the correlation coefficient ( $r$ ) was 0.90. However, there was a fair amount of scatter about the linear regression line (Figure 7). Subsequent evaluation of the first three quarters of data showed that the median ratio of the sum of HANs to TTHMs is 0.101 (the 25th percentile is 0.065, and the 75th percentile is 0.147). Thus, in general, HANs represented about one tenth of the concentration of THM. Another study found that the concentration of dichloroacetonitrile (DCA) averaged about 10 percent of the THM concentration.<sup>15</sup>

Some DBPs have a median value that is less than the compound's MRL value (Table 4). However, every individual DBP has been detected at some time in

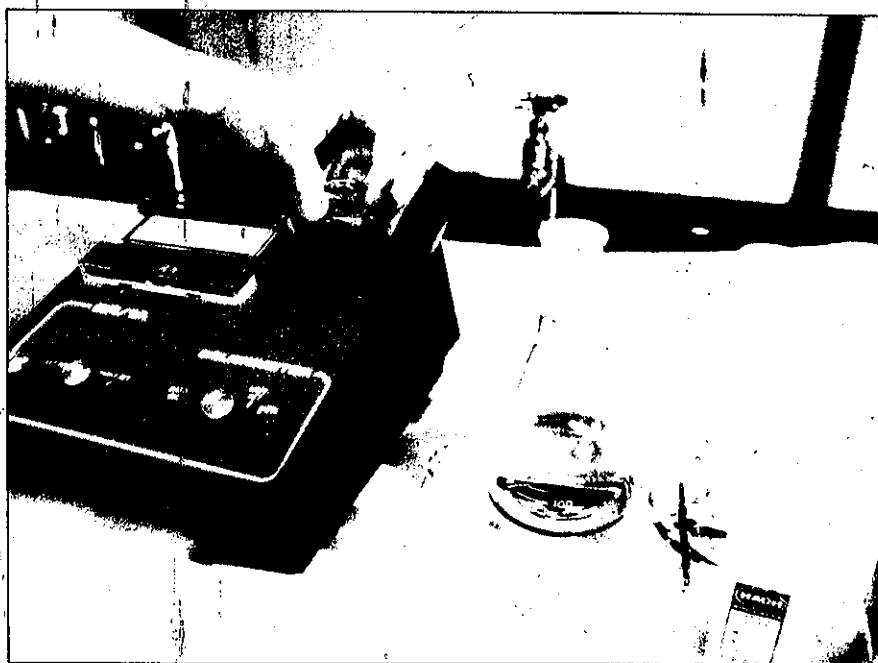
some utility's water. During the first sampling quarter, 2,4,6-trichlorophenol was detected at low levels at a few utilities, yet it was not detected in subsequent sampling quarters.

**Brominated DBPs.** During the first quarter of baseline sampling, a high correlation was found between dibromoacetic acid (DBAA) and dibromochloromethane ( $r = 0.91$ ). In addition, relatively high levels of the measured brominated DBPs were detected at some utilities. These findings suggested that the influence of bromide in the raw water should be evaluated; therefore, bromide and chloride analyses of the plant influents were added, beginning with the second quarter of baseline sampling.

Among the 35 utilities in this project, influent bromide levels ranged from  $<0.01$  to  $3.00$  mg/L. Table 5 shows DBP data for the utility with the highest bromide level (utility 10). Not only was there a shift in THMs to the more brominated species at high bromide levels, but the same situation existed for the HANs and HAAs. The TTHM levels of this utility were comparable with the median TTHMs of all 35 utilities studied, with the significant difference being the distribution of chlorinated and brominated THMs. Likewise, DCAA and TCAA, commonly found in other DBP studies<sup>16,17</sup> as well as this one, were barely detected at utility 10; instead, DBAA was the major HAA detected.

Table 6 shows DBP data for another utility (utility 12) with high bromide levels; however, for this utility there were seasonal shifts in the concentration. Such shifts were observed in many utilities as a result of drought conditions and saltwater intrusion. During the summer of 1988,  $0.41$  mg/L bromide was detected at utility 12. In the fall of 1988 and winter of 1989, higher bromide levels were detected ( $0.78$ – $0.79$  mg/L). As Table 6 shows, the change in distribution of brominated DBPs was consistent with the change in bromide level. For example, bromoform and dibromoacetonitrile (DBAN) represented (on a weight basis) 36 and 67 percent of the sum of their respective class fractions in the summer, when the bromide level was lowest. These percentages increased to about 66 and 85, respectively, in the fall and winter, when the bromide levels were higher.

As noted, the production of THMs at utilities with high bromide levels can shift to the more brominated species. The same phenomenon was observed for HAAs and HANs. It is fortunate that many brominated DBPs were included in the study; otherwise, the DBP levels of some utilities would have been misrepresented. Yet, research has shown that other brominated species exist that were not included in the analytical

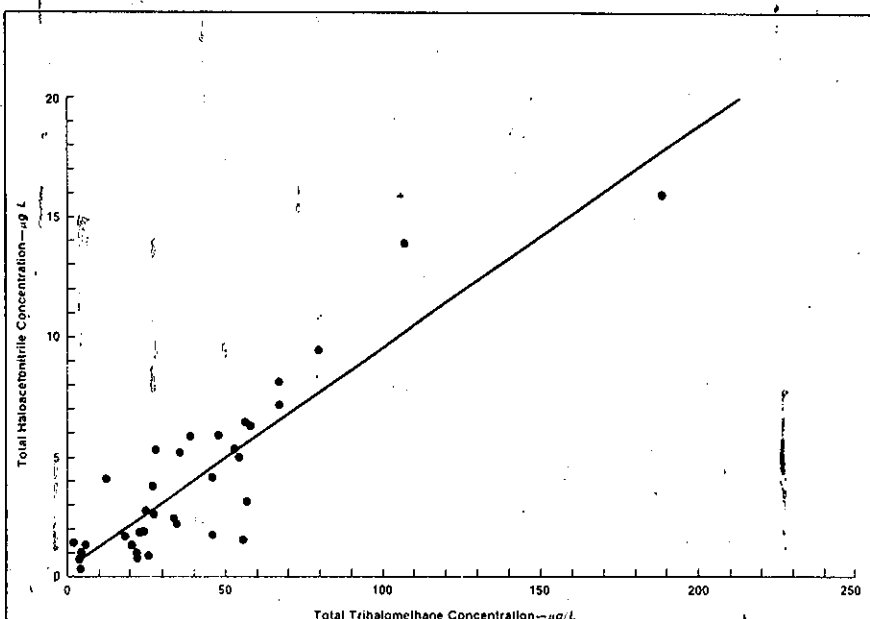


*In this study, plant effluent samples were analyzed for their chlorine residual concentration.*

methods for this DBP study. Analysis by GC-MS revealed the presence of HAAs containing both bromine and chlorine atoms,<sup>18</sup> as observed with THMs; however, analytical standards for these compounds were not available. Research also indicated the formation of brominated trihalonitromethanes in a manner similar to the production of CHP (trichloronitromethane).<sup>19</sup> These findings emphasize that brominated DBPs—not just chlorinated DBPs—are important in chlorinated drinking water.

**Cyanogen chloride.** Typically, chloramines are used as a means of reducing

THM levels in treated waters. During this DBP study, 14 of the 35 utilities surveyed utilized chloramines. Ten of these had free chlorine contact time prior to ammonia addition, and the remaining four added chlorine and ammonia concurrently. As shown in Figure 8, the median value of CNCl for utilities that used only free chlorine was  $0.4$   $\mu\text{g/L}$ . Utilities that prechlorinated and postammoniated had a CNCl median of  $2.2$   $\mu\text{g/L}$ . The 95 percent confidence intervals around the medians (not shown in this figure) indicate that these two disinfection schemes are statistically



**Figure 7.** Correlation of HANs with TTHMs for first quarter ( $n=35$ ,  $r=0.90$ )

different in regard to the CNCI levels detected in clearwell effluents. The other disinfection schemes shown in Figure 8 represent small data sets, making it difficult to interpret the data. Figure 9 was generated to show CNCI levels for utilities distributing chlorinated water compared with those distributing chloraminated water. Although the order of chemical addition was considered in Figure 8, this was not done in Figure 9. Again, the utilities that provide water with a free chlorine residual had a median CNCI value of 0.4  $\mu\text{g/L}$ , and the ones that deliver chloraminated water had a median value of 1.6  $\mu\text{g/L}$ . These treatment regimes are statistically different with regard to CNCI results.

Research in Japan<sup>20</sup> showed that CNCI was sometimes formed in the presence of certain amino acids and hypochlorous acid but was always formed in the presence of the amino acids tested when both hypochlorous acid and the ammonium ion (i.e., chloramines) were present. Other research<sup>21</sup> found that CNCI was formed by the reaction of humic acid with hypochlorous acid in the presence of the ammonium ion. CNCI was at a maximum when the reaction mixture contained a weight ratio (mg/L  $\text{Cl}_2$ :mg/L  $\text{NH}_3$ -N) of 8-9:1, and the maximum yield of CNCI increased as increasing amounts of hypochlorous acid were added. Furthermore, these formation patterns were reproduced with three raw waters in Japan. These data imply that CNCI may be more readily formed in chloraminated systems.

In other research endeavors, *N*-chloroglycine was formed as a result of the reaction of monochloramine with glycine under conditions typical for drinking water,<sup>22</sup> and it has been suggested that CNCI is formed by the reaction of glycine with chlorine.<sup>23</sup> Studies have demonstrated the formation of organochloramines by the use of inorganic chloramines in the treatment of water.<sup>24</sup> The CNCI results presented here, as well as the presence of moderate concentrations of TOX in chloraminated waters with low THM levels, indicate a need to further identify chloramine by-products.

**Aldehydes.** During the third quarter of baseline sampling, the median values for formaldehyde and acetaldehyde were 3.5 and 2.6  $\mu\text{g/L}$ , respectively. To determine whether these aldehydes were produced by the disinfectants and oxidants used at the treatment plant or whether they originated from the source water, e.g., from a biogenic process, 10 utilities were evaluated for aldehyde levels in their plant influents. Formaldehyde was found in one influent at 1.2  $\mu\text{g/L}$ . However, because MWD's holding studies determined that formaldehyde is unstable in water with no chlorine or chloramine residual present, formaldehyde levels in raw water may have been higher than

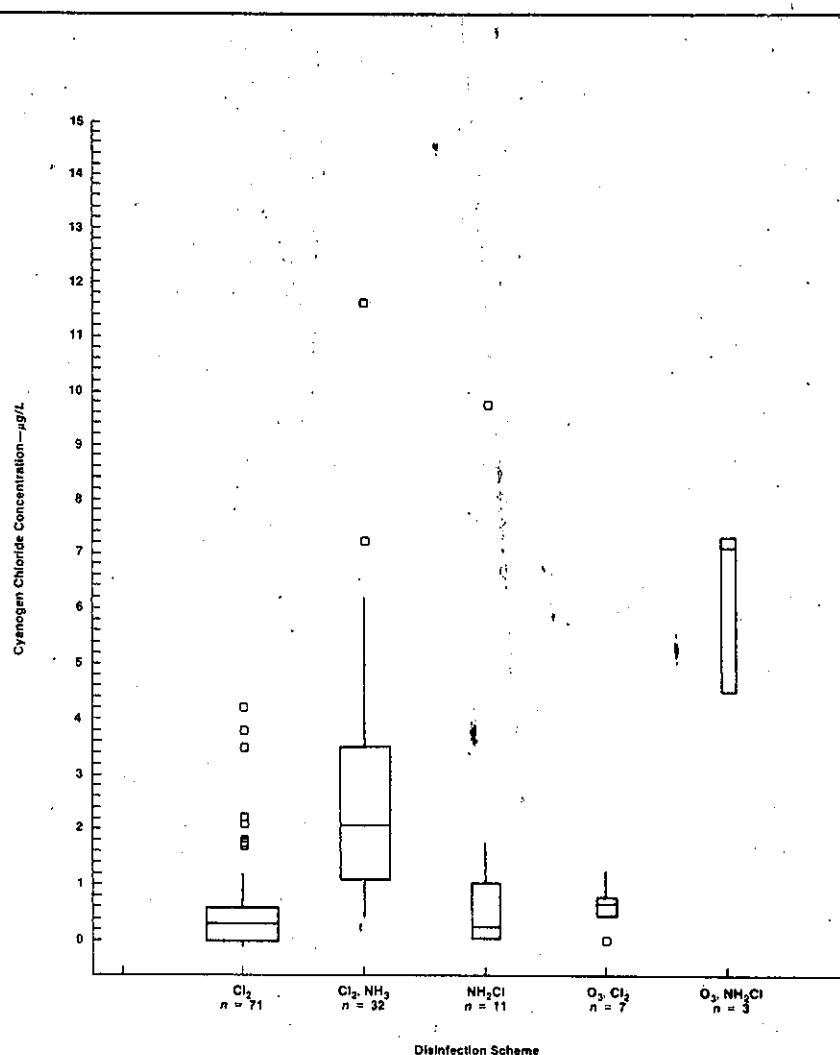


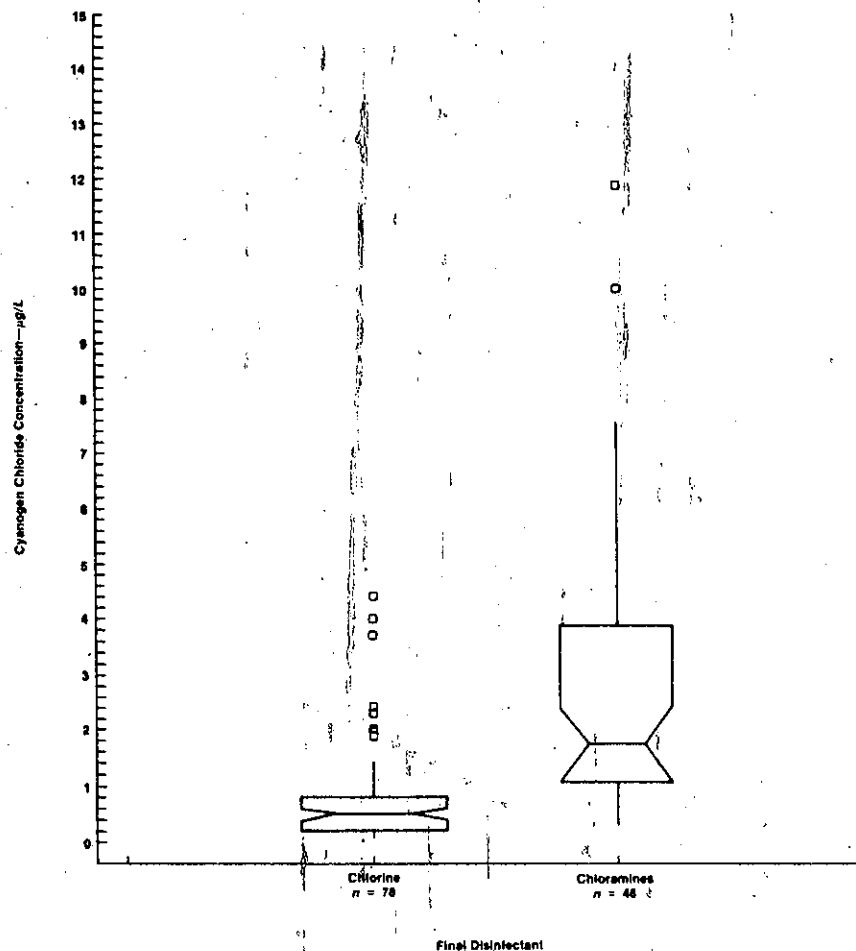
Figure 8. Box-and-whisker plot of CNCI by disinfection scheme (n—number of observations)

TABLE 6  
DBP concentrations at utility with seasonal change in bromide levels (utility 12)\*

Component	Summer 1988	Fall 1988	Winter 1989
Plant influent—mg/L			
Total organic carbon	2.6	2.2	2.8
Chloride	111	215	202
Bromide	0.41	0.78	0.79
Clearwell effluent—µg/L			
Chloroform	4.7	1.4	0.86
Bromodichloromethane	13	7.5	6.5
Dibromochloromethane	28	25	24
Bromoform	26	72	53
Total trihalomethanes	72	106	84
Trichloroacetonitrile	<0.012	<0.029	<0.029
Dichloroacetonitrile	0.74	0.24	0.19
Bromochloroacetonitrile	1.6	0.96	1.4
Dibromoacetonitrile	4.6	7.0	11
Total haloacetonitriles	6.9	8.2	13
Monochloroacetic acid	<1.0	<1.0	<1.0
Dichloroacetic acid	2.9	1.7	0.9
Trichloroacetic acid	1.6	1.2	0.8
Monobromoacetic acid	1.0	1.6	1.3
Dibromoacetic acid	14	17	13
Total haloacetic acids	20	22	16

\*Data for spring 1988 were not included because bromide was not measured that quarter.





**Figure 9.** Notched box-and-whisker plot of CNCl by final disinfectant (n—number of observations)

**TABLE 7**  
Aldehyde levels in plant influents and effluents\*

Utility	Formaldehyde—µg/L		Acetaldehyde—µg/L	
	Influent	Effluent	Influent	Effluent
Utility 9	3.9	8.7	4.4	6.1
Utility 14	6.4	4.1	2.4	4.5
Utility 22	1.2	4.3	<1.0	2.2
Utility 29	2.0	8.0	<1.0	4.6
Utility 30	<1.0	4.3	1.3	2.2
Ozone plants				
Utility 19	<1.0	7.5	<1.0	3.9
Utility 25	3.2	19	16	5.5
Utility 32	1.4	21	<1.0	2.1

\*Selected data shown for illustrative purposes

detected. Acetaldehyde was found in five of the ten plant influents at levels of 1.5–3.3 µg/L. Thus, the acetaldehyde found in the clearwell effluents of some plants was initially present in the influents.

To resolve the issue of aldehydes in the raw water, all 35 utilities were sampled at the plant influents during the fourth quarter of baseline sampling. Mercuric chloride was utilized as a preservative for fourth-quarter aldehyde sampling because experiments had indicated that it acts as a biocide to inactivate microorganisms capable of biodegrading organic compounds. Formaldehyde was found in 16 of the 34 influents analyzed at levels of 1.2–13 µg/L. The median level of formaldehyde in plant influents for all 34 utilities was <1.0 µg/L, and the median level for the 16 utilities in which formaldehyde was detected in the influents was 2.8 µg/L. Acetaldehyde was found in 12 of the 33 influents analyzed at levels of 1.1–16 µg/L, the median level of acetaldehyde in plant influents for all 33 utilities was <1.0 µg/L, and the median level for the 12 utilities in which acetaldehyde was detected in the influents was 2.0 µg/L.

Table 7 shows the aldehyde levels in selected plant influents and effluents. At the three ozone plants, it is clear that formaldehyde was a product of the oxidation-disinfection process. Acetaldehyde was also detected in these effluents; at utility 25, however, there was a higher level of acetaldehyde in the plant influent. The other plants shown in Table 7 employed either free chlorine only or chloramination with prechlorination. At some plants, no formaldehyde or acetaldehyde was detected in the plant influent, but these aldehydes were detected in the effluent. When these aldehydes were detected in the influent, they were either at a very low level compared with that detected in the effluent (e.g., utility 29 had 2.0 versus 8.0 µg/L formaldehyde in the plant influent and effluent, respectively) or at a level comparable with that detected in the effluent (e.g., utility 14 had 6.4 versus 4.1 µg/L formaldehyde in the plant influent and effluent, respectively). From these limited data, it appears that formaldehyde and acetaldehyde are present because of a combination of the effects of plant disinfection processes and influent water quality, the combination varying from one utility to another.

Table 8 lists the aldehyde levels at three ozone plants during baseline sampling and at four plants that utilized only chlorine or chloramines but had high formaldehyde levels (≥10 µg/L) during at least one sampling. The latter four utilities had 10 µg/L or more of formaldehyde at a time when they had close to 100 µg/L (or more) TTHMs. These data suggest that when a utility's

**TABLE 8**  
Levels of aldehydes and THMs in selected clearwell effluents

Utility	Formaldehyde— $\mu\text{g/L}$			Acetaldehyde— $\mu\text{g/L}$			TTHMs— $\mu\text{g/L}$		
	Summer 1988	Fall 1988	Winter 1989	Summer 1988	Fall 1988	Winter 1989	Summer 1988	Fall 1988	Winter 1989
Utility 2	10	8.2	NR*	4.2	4.4	NR	90	82	60
Utility 9	12	6.2	8.7	4.1	2.8	6.1	95	54	40
Utility 26	17	8.6	2.1	6.0	7.1	2.1	164	100	98
Utility 29	NR	13	8.0	4.3	5.2	4.6	109	180	259
Ozone plants									
Utility 19	5.8	10	7.5	4.8	5.3	3.9	15	20	5.9
Utility 25	31	22	19	15	9.9	5.5	34	16	9.0
Utility 32	30	24	21	3.5	2.8	2.1	3.1	1.4	0.72

\*NR—not reported; analytical problem

water quality and treatment practices produce a high level of THMs, they can potentially produce a high level of formaldehyde. Examination of the aldehyde levels at three ozone plants during baseline sampling indicates not only that a higher amount of formaldehyde was typically detected at these utilities, but also that the TTHM levels were relatively low. As discussed in a companion article by Jacangelo et al.,<sup>25</sup> there can be a trade-off of halogenated DBPs for formaldehyde in implementing ozonation.

**Surrogate for DBPs.** During this study, analyses were performed through four analytical fractions for a total of 19 individual halogenated DBPs (XDBPs). Concerns have been expressed about the practicality of performing several different DBP analyses in a utility's routine monitoring program, and the question of employing a surrogate has been raised. There was a strong correlation between TTHMs and the sum of XDBPs measured in this project ( $r = 0.96$ ) (Figure 10). Because THMs represent the largest DBP fraction detected in this study, the data were reevaluated by comparing TTHMs to the sum of non-THM XDBPs. In this instance,  $r$  decreased to 0.76. However, the latter comparison does not mean that THMs cannot be used as a surrogate or predictor of the total of all XDBPs. The correlation between TTHMs and  $\text{XDBP}_{\text{sum}}$  is significant because it suggests that control of a utility's THMs may reflect control of the other DBPs overall. Although this trend holds true for the sum of XDBPs, it does not hold true for individual compounds; e.g., comparing TTHMs to HKs yields an  $r$  of only 0.06. In addition, other individual DBPs may require separate monitoring based on their health effects and their formation and control relative to THMs, e.g., THM production can be minimized by using chloramines, whereas CNCl formation can be increased.

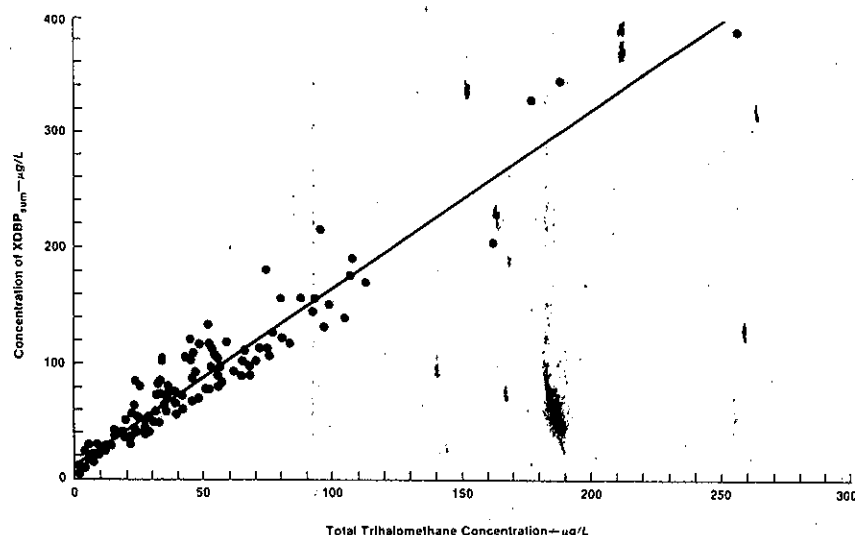
Analysis for TOX was also evaluated as a surrogate for individual DBP anal-

yses. One issue associated with the use of TOX as a surrogate analysis is the percentage of TOX in chlorinated waters that is accounted for by compounds for which analytical methods exist and are economically feasible. In another DBP study,<sup>26</sup> this percentage was between 30 and 60 percent; the remaining TOX was not measured or quantified by current analytical methodologies. The amount of TOX in samples studied in this 35-utility survey indicated that, based on mean data, 25 percent of the TOX (on a molar basis) was accounted for by the individual DBPs measured in the laboratory. However, the percentage of TOX accounted for by the target compound DBP analysis ranged from 2 to 75 percent.

Figure 11 shows that the correlation of the sum of XDBPs measured with TOX (on a molar halide basis) during the second sampling quarter had an  $r$  of 0.56. Similarly, the correlation of TTHMs with TOX had an  $r$  of 0.54. It proved

infeasible to dechlorinate the TOX samples in the field, and concern over further TOX production during overnight shipping under iced conditions prompted several experiments. These tests indicated that TOX values were not affected for chloraminated samples but that there was some TOX production during the shipping of chlorinated samples, the amount of which was site-specific. Therefore, in Figure 11, the chloraminated waters are noted specifically. When data for only the utilities that chloraminated were used, the correlation improved. However, the correlation between XDBPs and TOX is not as good as that between XDBPs and TTHMs. In addition, not enough is understood about the other components of TOX, making its use as a surrogate difficult. However, the TOX test can be valuable as a complementary analysis to individual DBP measurements.

Several researchers have investigated the relationships among TOC, UV, and



**Figure 10.** Correlation of halogenated DBPs with TTHMs for four quarters ( $n=140$ ;  $r=0.96$ )

pH	7.3	8.1	9.0	9.0	8.9	8.9	9.0
Total chlorine residual—mg/L	4.0	4.0	3.5	2.9	3.2	3.5	3.5
DBP concentration—µg/L							
TTHMs	38	38	39	55	46	37	44
Total HANs	5.0	4.8	1.5	0.72	0.51	0.57	0.49
1,1-Dichloropropanone	2.2	2.2	0.77	0.69	0.41	0.38	0.32
1,1,1-Trichloropropanone	1.5	1.4	<0.013	<0.013	<0.013	<0.013	<0.013
CHP	0.09	0.10	0.17	0.20	0.17	0.16	0.18
CH	4.0	3.9	1.2	0.95	0.64	0.61	0.47
Total HAA5	34	35	39	39	44	44	44
DCAA	18	19	22	22	25	26	26
CNCI	4.3	4.5	3.6	2.0	1.7	1.0	1.3
TOX	180	200	150	150	140	150	150

\*FI—filter influent; FE—filter effluent; CE—clearwell effluent; L1-L4—distribution system locations in order of increasing residence time  
†No lime added

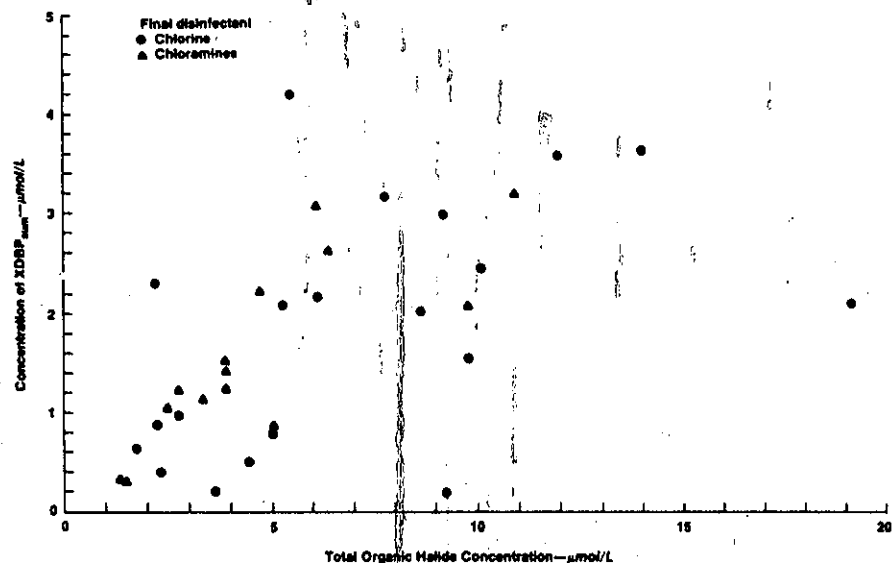
THM formation potential (THMFP).<sup>27-29</sup> During the second quarter of sampling, the correlation between the UV and TOC of plant influents was high, i.e.,  $r = 0.92$ . However, neither of these two parameters correlated with the TTHMs in the plant effluents. That is, during the last three sampling quarters, for effluent THMs versus influent TOC,  $r = 0.48$  (Figure 12); for THMs versus UV,  $r = 0.41$ . Because utilities apply chlorine dosages based on numerous considerations, e.g., the chlorine demand of the water and taste-and-odor control, the THMs detected do not necessarily reflect the THMFP of that water. Also, because a large percentage of the utilities in this study used chloramines and several utilized ozone as a preoxidant, it is not surprising to find a poor correlation between the influent TOC and the effluent DBPs. A mathematical model that accounts for chlorine dosage, TOC concentration, bromide level, temperature, pH, and other parameters is currently

being explored to determine whether THM levels are predictable.<sup>28</sup>

One approach to THM control has been to optimize coagulation for precursor removal,<sup>30</sup> and TOC has been used as a surrogate for THM (and DBP) precursors. Ideally, precursor removals of 50–75 percent are desirable.<sup>30</sup> However, costs associated with higher alum dosages and increased solids loading, removal, and disposal are being evaluated.<sup>31</sup> During the second and third sampling quarters of this DBP study, the mean TOC removal for utilities with filtration capabilities was 24 percent from the plant influent to the clearwell effluent. The mean removal prior to filtration was 20 percent, indicating that the filtration process provided only a small part of the overall removal. Furthermore, when a correlation of TOC removal from plant influent to clearwell effluent was evaluated against influent TOC levels, a correlation of only  $r = 0.59$  was obtained. For utilities with influent TOC levels of

$\leq 5$  mg/L, overall TOC removal through the plants varied from 1 to 50 percent. In another study of five conventional treatment plants,<sup>32</sup> average TOC removal prior to filtration was 11 percent, and average removal overall was 15 percent. These results indicate that TOC removal is ineffective under treatment practices at most of the utilities in this study. As part of the second year of the DBP study, selected utilities are performing treatment studies to minimize DBP formation. Two of the 35 utilities will experiment with optimized coagulation for TOC and DBP precursor removal.

**Distribution system sampling.** Tables 9 and 10 show DBP data over time for two chloraminated distribution systems—utilities 25 and 6. Although utility 25 used lime addition for stabilization, lime was not being added when the plant filter influent and effluent were sampled. As a result, these two samples had pH values of 7.3–8.1, but with lime addition, the clearwell effluent and distribution sampling points had pH values of 8.9–9.0. Previous studies<sup>33-35</sup> indicated that high pH values (around 9) result in increased formation of THMs and decreased formation of TCAA, DCAN and other HANs, CH, TOX, and 1,1,1-trichloropropanone. These studies demonstrated that DCAN, CH, and 1,1,1-trichloropropanone can all undergo base-catalyzed hydrolysis. When the DBP data from the filter effluent and clearwell effluent at utility 25 are compared, it is apparent that the HANs, HKs, and CH are significantly diminished at the higher pH. In addition, these compounds further degrade throughout the distribution system. However, at utility 6, where lime addition was not practiced and the pH of the water was from 7.5 to 8.0, these DBPs were stable throughout the system. The levels of THMs and these unstable DBPs were comparable at utilities 6 and 25 when lime was not added at the latter utility. These data and the referenced studies

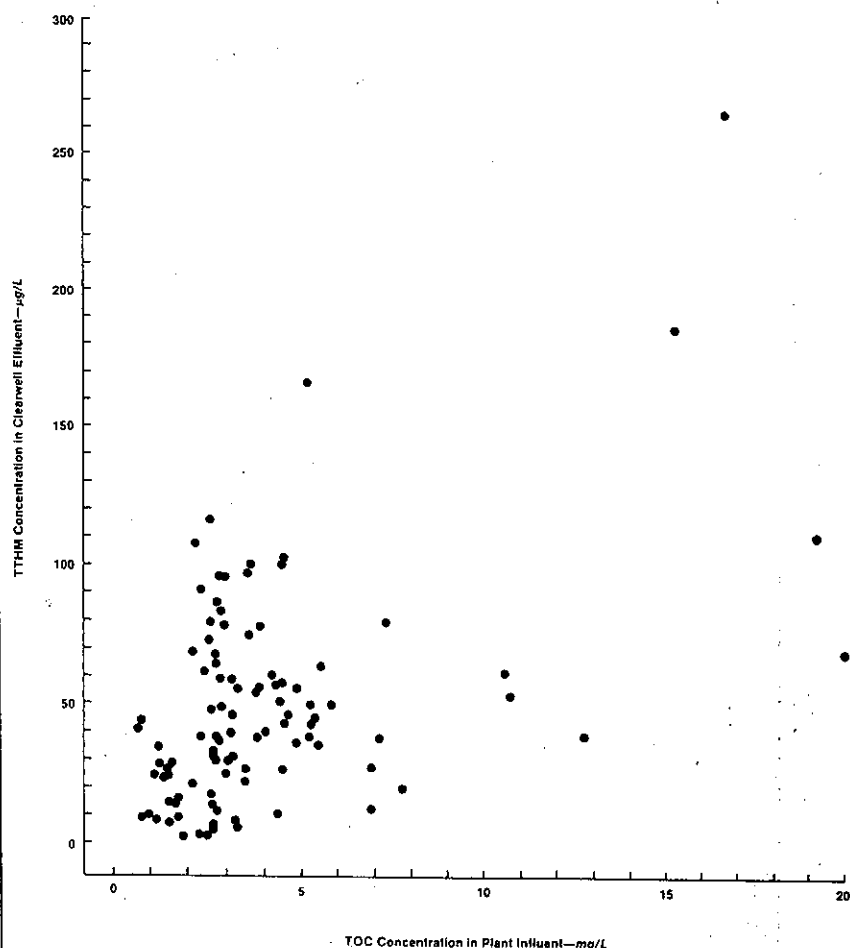


**Figure 11.** Correlation of halogenated DBPs with TOX on a molar halide basis for second quarter ( $n=34$ ;  $r=0.56$ )

**TABLE 10**  
Effects of residence time on DBP formation at utility 6

Parameter	Sampling Location*				
	CE	L1	L2	L3	L4
Water quality					
pH	8.0	7.7	7.6	7.5	7.9
Total chlorine residual—mg/L	3.5	>2.0	>2.0	2.0	>2.0
DBP concentration— $\mu\text{g/L}$					
TTHMs	44	51	50	53	50
Total HANs	6.3	7.4	6.8	6.3	7.7
1,1-Dichloropropanone	1.2	1.3	1.2	1.3	1.4
1,1,1-Trichloropropanone	2.3	2.4	2.4	1.8	2.2
CHP	0.44	0.56	0.50	0.49	0.59
CH	4.5	5.1	4.9	4.7	5.2
Total HAAs	40	47	45	34	46
DCAA	20	23	21	15	22
CNCl	4.7	7.5	NA†	6.0	9.9
TOX	240	250	250	220	240

\*CE—clearwell effluent; L1-L4—distribution system locations in order of increasing residence time  
†NA—Not analyzed



**Figure 12.** Plot of TTHMs in clearwell effluent versus TOC in plant influent for three quarters ( $n=105$ ;  $r=0.48$ )

imply that an increase in pH can degrade or hydrolyze certain DBPs; however, the higher pH can increase THM formation.

Finally, CNCl decreased in the distribution system of utility 25 but increased in utility 6's system (Tables 9 and 10). The increase at the latter utility was probably caused by the continuing reaction of chloramines with CNCl precursors. The decrease at utility 25 may have resulted from degradation of CNCl at high pH. In a study of CNCl stability,<sup>36</sup> reagent water was buffered at pH values of 5, 7, and 9. CNCl broke down immediately at pH 9 and after three days at the other pH levels. However, CNCl in unbuffered reagent water was stable, implying that the buffers may have caused the degradation. More fundamental research into the formation and stability of this DBP is needed.

### Summary and conclusions

The median TTHM value for this DBP study was  $39 \mu\text{g/L}$ , which was also the overall TTHM median of a recent AWWARF national THM survey. Furthermore, the current 35-utility DBP study represents the same THM distribution as the 727-utility AWWARF survey. The THMs were the largest class of DBPs measured in this study (on a weight basis). The next significant DBP fraction was HAAs; the median  $\text{HAA}_{\text{sum}}$  was  $19 \mu\text{g/L}$ . When the DBP data were evaluated for correlations among various parameters, TTHMs were found to have a high correlation with the sum of the halogenated DBPs.

Of the 35 utilities in the baseline study, only three employed ozone, yet almost all had detectable levels of formaldehyde and acetaldehyde. Although these aldehydes were present in some of the plant influents, chlorination alone has been demonstrated to produce formaldehyde and acetaldehyde.

Chloramines have been used effectively to limit the formation of THMs and other DBPs, but, in most waters, CNCl was found to increase in the presence of chloramines. The distribution of CNCl was statistically demonstrated to be divided into two groups, depending on whether the final disinfectant was chlorine or chloramines.

Bromide in source waters has been shown to shift the distribution of THMs, HANs, and HAAs to the more brominated species. A high pH (around 9) has been implicated in the degradation of HANs, HKs, CH, and possibly CNCl. The findings of this and other DBP studies indicate that a complex set of equilibria and kinetics is involved in understanding DBP formation and degradation. To quote a remark attributed to the naturalist John Muir, "When we try to pick out anything by itself, we find it hitched to everything else in the universe."

The work produced by this study is



leading to identification of the DBPs that can be expected in drinking water as a function of source water quality, seasonal factors, water treatment process selection, operation, and disinfection processes and chemicals. The results of this study will be of value to both (1) the USEPA in defining the best available technology when setting new THM and DBP regulations and (2) the water utility industry in deciding among treatment process alternatives to meet new DBP regulations.

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